

Renewable Energy Source using Pressure Driven Filtration Processes and Systems.

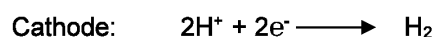
Field of the Invention.

The present invention relates generally to the production of a renewal energy source, in particular hydrogen, using pressure driven filtration processes and systems.

Background

The development of renewal energy sources is becoming increasingly important to address global warming and other environmental issues. Hydrogen is a good energy carrier for energy storage and hydrogen burns to produce water, with zero CO₂ emissions. Thus, the efficient production and storage of hydrogen for energy generation is a very attractive proposition.

Water electrolysis technologies are known for producing hydrogen from water. Water is the reactant, which is dissociated to hydrogen and oxygen using a direct current.



A number of different types of water electrolysis processes have been investigated for hydrogen production including alkaline water electrolysis, proton exchange membrane water electrolysis, solid oxide water electrolysis and alkaline anion exchange membrane water electrolysis.

The satisfactory scale up of hydrogen generation may be hindered by a lack of a suitable source of water, a renewable energy source and/or a convenient location for storage of the hydrogen produced.

It is the aim of the present invention to provide an improved devices, processes and systems for hydrogen generation that address some or all of these issues.

Summary of the Invention

According to a first aspect of the present invention there is provided a membrane element configured for osmotic and/or gauge pressure driven filtration of water and electrochemical splitting of at least a proportion of the water for the co-generation of hydrogen, the membrane element comprising at least one selectively permeable membrane configured to least partially purify feed water when a pressure difference is provided across the membrane, wherein the membrane element includes at least one anode electrode and at least one cathode electrode.

In the context of this disclosure, the selectively permeable membrane is any type of reverse osmosis (RO) or ultrafiltration (UF) type membrane that may be used for osmotic and/or gauge pressure driven filtration of water. "RO" type of membrane includes those membranes used for reverse osmosis, pressure retarded osmosis (PRO), forward osmosis (FO) and nanofiltration (NF). "UF" type of membrane includes those membranes used for ultrafiltration (UF), microfiltration (MF) and other purification from suspended solids processes. These types of membranes are selectively permeable with a maximum pore size of 0.1 microns. In this respect, the type of membrane will have a particular pore size, for example MF membranes generally have a maximum pore size of about 0.1 microns; UF membranes generally have a pore size of 0.01 to 0.1 microns; NF membranes generally have a maximum pore size of 0.01 microns and RO membranes generally have a pore size of 0.0001 microns. However, other parameters may be used to characterize these types of membranes as is known in the art.

The membrane element of the first aspect is preferably incorporated into a module configured for pressure driven filtration of water and electrochemical splitting of at least a proportion of the water for the co-generation of hydrogen. To this end, a second aspect of the present invention provides a module comprising:

a feed water inlet;

at least one membrane element according to the first aspect of the invention; and

a product water outlet and optionally a reject water outlet.

The optional reject water outlet is for the reject flow which is the part of feed water which does not pass the membrane, being rejected as brine in selectively permeable membrane application. This reject flow may not exist in UF and MF applications.

Additionally, the module may be provided with a hydrogen and/or oxygen outlet. However, more preferably, dissolved hydrogen is provided in the reject flow or product water for later extraction therefrom, for example by degasification or gas separation membranes.

The membrane element according to the first aspect of the present invention and the module according to the second aspect of the invention may be incorporated into any pressure driven water filtration process or system to provide simultaneous co-generation of at least partially purified water and hydrogen.

Accordingly, a third aspect of the present invention provides a process for pressure driven water filtration with co-generation of hydrogen, the process comprising:

supplying feed water from a feed water inlet to a membrane element according to the first aspect of the present invention;

applying a pressure differential across the RO and UF type selectively permeable membrane of the membrane element to draw feed water through the membrane to form a product water;

applying a potential difference between the electrodes of the membrane element to cause electrochemical splitting of at least a portion of the feed and/or product water for formation of hydrogen and oxygen; and

collecting the product water and optionally a reject flow, and hydrogen.

Preferably, the hydrogen is dissolved in at least one of the product water or reject flow for subsequent extraction therefrom, for example by degasification or membrane gas separation.

A fourth aspect of the present invention provides a system for pressure-driven water filtration with the co-generation of hydrogen, the system comprising:

- a feed water inlet;
- at least one membrane element according to the first aspect of the present invention;
- at least one pump to apply a pressure to the feed water;
- a power source to provide a potential difference to the electrodes of the membrane element;
- a product outlet and optionally a reject water outlet; and
- a hydrogen outlet within the product and/or reject water.

In embodiments, the membrane element and module of the first and second aspects of the invention respectively may form part of a pressure retarded osmosis (PRO) system to provide electricity from the water with the co-generation of hydrogen. However, more preferably, the membrane element or module is incorporated into a reverse osmosis (RO) or Nano Filtration (NF) or other brand name system for the desalination of water and co-generation of hydrogen.

Alternatively, the element or module may be incorporated into any other water filtration system, such as ultrafiltration or microfiltration systems, to provide purified water and hydrogen generation, all of which are discussed further herein. The main difference between RO; PRO; NF from UF and MF is that RO; PRO; NF implement salt rejection semipermeable membrane and have a reject flow. The UF and MF membrane are not salt rejection semipermeable and do not have reject flow. However, all may be provided with electrodes within or on their membranes to allow water splitting in accordance with the invention.

In the context of this disclosure, reverse osmotic (RO) separation processes where semipermeable salt rejection layer is included in the membrane extends to Reverse Osmosis (RO); Nano Filtration (NF) and any other salt rejection semipermeable membranes in which RO dissolved ion separation process take place. Pressure Retarded Osmosis (PRO) processes where semipermeable salt rejection layer is included in the membrane applies to any processes where the semipermeable membrane may act as an osmotic pump and low salinity water penetrates into high salinity water. This is a different physical process than RO dissolved ion separation process and also applies to Forward Osmosis (FO), and any other processes wherein the membrane acts as osmotic pump

Water filtration processes and systems of the present invention include Ultra Filtration (UF) and Micro Filtration (MF) and other processes based on non- salt rejection semipermeable membranes in which water is moving through any membrane driven by gauge pressure for purpose of water treatment (purification from suspended solids), and hydrogen generation is a complementary co-generation activity. In present invention membrane implemented for UF, MF and other purification from suspended solids processes will be mentioned in one general name "UF type membrane"

The particular number and arrangement of inlets and outlets provided within an embodiment of a module, process or system of the invention is dependent upon the type of desalination or water treatment process in relation to which the electrochemical splitting of water is incorporated. For RO; NF processes, the module has one inlet "Raw saline solution" and two outlets: "residual brine stream" ("reject flow" or "reject outlet") and a "Permeate stream". Hydrogen can go out from one or both of these outlets.

The module for a PRO process has two inlets and two outlets. An inlet for "Draw Solution" and for "Feed water" and two outlets, an outlet for "Residual fluid stream" and an outlet for "Residual brine". Hydrogen may go out from one or both of these outlets.

In contrast, for UF and MF processes, the module usually has one inlet "Feed Water" and one outlet "Filtrated Water". Hydrogen can go out from only one outlet.

In all of the aforementioned systems and processes, only a small proportion of the water involved in RO; NF; PRO; UF; MF is subject to electrochemical splitting to form hydrogen within the membrane, with the remainder producing the product or filtrated water or the rejected draw solution. Preferably, less than 5% of the above mentioned water is split. More preferably, for all processes the amount is less than 1 %; especially 0.05%, or more especially 0.01% or ideally less than 0.01%.

The membranes, modules, systems and processes according to the invention should be provided with an appropriate power source to enable a current to be applied across the electrodes to enable electrochemical splitting of the water to occur. Preferably low current densities are used, preferably below 100 mA/cm², more preferably below 10 mA/cm²; especially below 5mA/cm², ideally below 1 mA/cm².

The process may also provide for pH correction to optimize the reaction taking place across the electrodes, for example to decrease the reversible potential of oxygen evolution reaction.

It is to be appreciated that any type of RO and UF type membrane may be provided within the module for carrying out osmotic and/or gauge pressure-driven filtration of the feed water. However, the membrane is adapted to include an anode and cathode and as an option an additional electrode to allow for electrochemical split of part of the penetrated water to generate hydrogen. Suitable membranes incorporating these electrodes may be provided in a very wide range of configurations and are not limited to the specific permutations disclosed herein.

For example, in one embodiment, the module comprises at least one RO type membrane comprising a salt rejection layer and a support layer, the membrane including at least one anode electrode and at least one cathode electrode, the electrodes comprising the salt rejection layer and/or being provided in, on or between one or both the salt rejection and support layers.

In embodiments, the membrane element or module may incorporate feed and/or permeate spacers. The electrodes may be provided on or adjacent one or other of the feed and/or permeate spacers.

The salt rejection layer, support layer, feed or permeate spacers serve to act as mechanical supports for the electrodes. Thus, the existing permeate and feed spacers of RO, PRO; NF, and FO modules, as well as semipermeable layers of RO; PRO; NF, and FO membranes can be used as is for separation of the anode and cathode electrodes incorporated into the membrane elements of the invention.

In UF type membrane the cathode and anodes may be positioned on either one or both inside and/or outside of these hollow-fibres membranes.

The electrodes may be incorporated into the RO type membrane in many different configurations. For example, the at least two electrodes may be provided between the salt rejection and the support layers. Alternatively, at least one electrode may be positioned between the salt rejection layer and the support layer and at least one electrode may be provided on an external surface of the salt rejection layer. In another embodiment, the at least two electrodes may both be provided on an external surface of the salt rejection layer.

In yet another embodiment the electrodes may be located on permeate and/or feed spacers, more preferably the electrodes are positioned on either side of the permeate or feed spacer. In alternative embodiments, both electrodes may be located on one side of permeate and/or feed spacers. In other embodiments, one electrode may be located on one side of permeate and/or feed spacers and the other electrodes may be located on opposite site of permeate and/or feed spacers.

In alternative embodiments of the present invention, the electrode (anode and/or cathode) may be coupled to the permeate or the feed spacer. Preferably, the feed spacer is mechanically coupled to the permeate tube. In one embodiment, the anode may be coupled to the feed spacer and the cathode may be coupled to the permeate spacer. In an alternative embodiment, the cathode may be coupled to the feed

spacer and the anode may be coupled to the permeate spacer. In yet other embodiments, the polarity of the spacers may be alterable so as to control which electrode is utilized as the cathode and which as the anode.

In other embodiments, the electrode (anode and/or cathode) may comprise the feed and/or permeate spacer. In such embodiments, the spacer is at least partially coated with an electrically conductive layer and/or a catalytic layer, thereby making the electrode electrically conductive and electrocatalytically active as anodes (for O₂ evolution) or electrocatalytically active as cathodes (for H₂ evolution) or both.

The spacers may be at least partially coated with at least one catalyst, for example being selected from Pt, Ir and any combination thereof.

The conductivity of the spacers may be obtained via, for example, coating of the polymer spacer with a nickel or copper metal and then displacing these metals with a Pt- or Ir-group catalyst, for example by redox displacement or other techniques.

In embodiments, the electrodes may be provided in the form of a grid or parallel spaced apart strips. Alternatively, the electrodes may be provided in the form of a full or partial coating of the permeate and/or feed spacer.

Furthermore, the salt rejection layer or spacers may be formed of a material that may allow them to serve as one of the electrodes, i.e., of a material having sufficient conductivity (such as e.g., graphite, composite of polymer and conductive particles, or metals).

More preferably still, the at least one electrode may be formed from graphene. In one embodiment, the electrode (anode and/or cathode) is graphene or carbon fiber/carbon cloth.

Preferably, the carbons are substrates for coating with mixed metal oxides (MMO) selected from platinum (Pt), iridium (Ir), Pt-Ir, ruthenium (Ru) metals and any

combinations thereof. In these embodiments, the MMO/C electrodes may be prepared by a two-step process comprising forming a sacrificial copper or nickel layer on the carbon via electroless or electrodeposition and displacing the sacrificial metal by Pt, Ir, Ru or Pt-Ir.

In embodiments, the salt rejection layer may be formed from graphene and comprise one of the electrodes. The support layer is preferably comprised of a porous material, preferably being a ceramic material.

Alternatively, the electrode (anode and/or cathode) may be a titanium material to enhance durability.

The electrode may be provided in any configuration but is preferably selected from the group consisting of a mesh, plate, cloth formed of fiber and a sintered body, more preferably being made of titanium.

The semi-permeable membrane may further comprise a reference electrode. Optionally, at least one dielectric material may be provided between the at least two electrodes. The feed and/or permeate spacers may act as a dielectric material for the electrodes printed, coated or located on each side of the spacer(s).

Additionally, at least one catalyst may be provided on at least one or both of the electrodes to enhance the desired reaction, for example to facilitate oxygen and hydrogen generation and hamper chlorine evolution.

In one embodiment, the electrode may be at least partially coated with at least one catalyst. Preferably, the catalyst is selected from at least one of the group consisting of iridium oxide, ruthenium oxide, tantalum oxide, titanium oxide, platinum, and platinum oxide, and any combination thereof.

As mentioned above, the process and system according to the third and fourth aspects of the invention may be applied to many different types of pressure driven water filtration processes and systems.

In a preferred embodiment, the process and system comprise a reverse osmosis (RO) process and system for splitting water to hydrogen and oxygen in an osmosis separation module comprising at least one, preferably multiple membrane elements, said membrane having a feed side and permeate side with the at least two

electrodes positioned on the RO type membrane, and/or support layer, and/or feed and/or permeate spacers of the membrane element. Raw saline solution is delivered to the module and a part of the raw saline solution exits the module as a residual brine stream, part of the raw saline solution penetrating the membrane in a normal reverse osmosis process to produce desalinated water by a net driving force of the balance of the gauge and osmotic pressures and exiting from a permeate side of the membrane element as a permeate stream.

The process includes applying continuously, or for a predetermined period, electrical current to membrane electrodes, which causes part of the raw saline solution and/or permeate stream to be split into hydrogen and oxygen gases for evacuation from the osmosis separation module together with the residual brine stream and/or permeate stream. Thus, the RO module combines desalination of raw saline solution for commercial use with the simultaneous splitting of water into hydrogen and oxygen. Preferably, less than 5% of raw saline solution is used for hydrogen generation, more preferably less than 1%.

Alternatively, the process and system may be applied to a water purification process conducted on non-salt rejection semipermeable membrane such as Ultra Filtration and Microfiltration membrane in UF or MF process. In this embodiment, less than 1% of filtered water is used for hydrogen generation, preferably less than 0.1% of filtered water.

Such a process and system for providing filtration of water and cogeneration of hydrogen may include a suspended solids fouling filtration module, said membrane element having a feed side and filtered side with at least two electrodes positioned on the membrane, and/or the support layer, and/or the feed and/or filtered water spacers, wherein a raw saline solution enters the feed stream side of the module, and at least partially penetrates the membrane in a normal filtration process by a driving force of the gauge pressures and exits from the filtered side as a filtered stream, said method for splitting water to hydrogen and oxygen comprising: applying continuously, or for a predetermined period, electrical current to the electrodes, which cause part of the permeate stream to be split into hydrogen and oxygen gas for evacuation from the filtration module together with the filtered water stream.

In another embodiment, there is provided an osmotic process and system for the splitting of water to hydrogen and oxygen comprising delivering first and second solutions of different osmotic and gauge pressures to opposing sides of a RO type semi-permeable membrane to create a low salinity solution across the membrane; the semi-permeable membrane including at least two electrodes; applying a current across the electrodes of the RO type semi-permeable membrane to split the low salinity solution into hydrogen and oxygen; and collecting the hydrogen and oxygen.

Generally, the first solution is known as the draw solution and the second solution is known as the feed solution. For example, the feed solution may comprise sea water, brackish water, wastewater or fresh water, such as river or ground water.

The osmotic process may comprise pressure retarded osmosis or forward osmosis wherein the RO type semi-permeable membrane has a first side and a second side opposite the first side; a first saline solution comprising the draw solution having an osmotic pressure PO_r and a gauge pressure PG_r for entering the first side of the membrane; a second saline solution comprising a feed solution having an osmotic pressure PO_p and a gauge pressure PG_p for entering the second side of the membrane; at least part of the feed solution from the second side of the membrane penetrating to the first side according to a net driving pressure defined by the balance of pressures PG_r , PO_r , PO_p and PG_p ; wherein the draw solution and the penetrated part of the feed solution exit as a residual brine stream from the first side of the membrane via a residual brine outlet; a remainder of the feed solution at least periodically exits as a residual fluid stream from the second side of the membrane via an outlet and wherein at least part of a low salinity solution stream passes from the second side to the first side for splitting into hydrogen and oxygen as it passes across the semi-permeable membrane.

Additionally, or alternatively, at least part of the first saline solution and/or the second feed solution that passes along membrane goes for splitting into hydrogen and oxygen as it passes along the semi-permeable membrane.

It is to be appreciated that the processes and systems according to the third and fourth aspects of the invention may, and preferably do, incorporate conventional steps and components for carrying out these processes and systems that are used in

the prior art processes and systems. For example, intake and discharge channels, pre- and post-treatment units; pumps, control valves, delivery pipes and control units.

Preferably, the energy for operation of the process and system is produced efficiently. For example, the electricity for operation of the electrodes of the membrane may be provided using pressure retarded osmosis wherein the draw solution is provided by dissolving rock salt in salt domes. The dissolution of rock salt may be carried out under pressure, equal or near to PGr. Alternatively, dissolution may take place under atmospheric pressure. It is to be appreciated that the salt domes may also be used to store the hydrogen generated by the process.

Alternatively, the generated hydrogen may be stored in holding tanks for later use or fed into a network grid for use.

Brief Description of the Drawings

For a better understanding of the present invention and to show more clearly how it may be carried into effect, reference will now be made by way of example only to the accompanying drawings in which:

Figure 1A is a schematic diagram illustrating the principle of alkaline water electrolysis according to the prior art;

Figure 1B is a schematic diagram illustrating the principle of proton exchange membrane (PEM) water electrolysis according to the prior art;

Figure 2A is a schematic top view of a section through FO or PRO semi-permeable membrane incorporating electrodes according to an embodiment of the present invention;

Figure 2B is a three-dimensional view of the semi-permeable membrane shown in Figure 2A, with the salt rejection layer 4 and feed 7 removed;

Figure 3 is a three-dimensional view of a semi-permeable membrane incorporating a pair of electrodes according to an alternative embodiment of the present invention;

Figure 4 is a three-dimensional view of a semi-permeable membrane incorporating a pair of electrodes according to yet another embodiment of the present invention;

Figure 5 is a three-dimensional view of a semi-permeable membrane incorporating a pair of electrodes according to still yet another embodiment of the present invention;

Figure 6A is a fragmented three-dimensional view of a semi-permeable membrane having permeate and feed spacers and incorporating electrodes according to yet a further embodiment of the present invention;

Figure 6B illustrates two membranes according to Figure 6A arranged in mirror symmetry;

Figure 7 is a schematic diagram of a seawater desalination plant and process scheme in which one or more semi-permeable membranes according to the invention may be incorporated;

Figure 8 is a graph of reversible potentials for chlorine evolution, oxygen evolution and hydrogen evolution reactions as a function of pH. $T = 25^{\circ}\text{C}$, $[\text{Cl}^-] = 20 \text{ g/L}$ fugacity of gases = 1, no complexation, infinite dilution;

Figure 9 is schematic diagram illustrating an embodiment of a system of the present invention for hydrogen generation and storage;

Figure 10 is a schematic diagram of a permeate tube with a pair of spacers and electrodes coupled thereto according to an embodiment of the invention; and

Figure 11 is a schematic diagram of a permeate tube with multiple spacers and electrodes coupled thereto according to another embodiment of the invention.

Figure 12 is a schematic diagram of a Titanium foil cladding 300 to permeate and/or feed spacers with and without additional electricity conductors between titanium foil and plastic spacer.

Detailed Description

The present invention relates generally to the novel generation of hydrogen from water produced during water desalination or water treatment processes that use RO or UF-type membranes, wherein feed water is pressure driven (for example by osmotic and gauge pressures) against the membrane to allow certain components to pass through the membrane while other components are rejected, with a proportion of the water being split electrochemically to produce hydrogen.

In some instances, the process utilises feed water penetrated via RO type semipermeable membrane in to draw solution during pressure retarded osmosis process PRO, or forward osmosis FO. The very low salinity water passes via the RO type semi-permeable membrane from feed stream to draw solution stream. A small portion of this very low salinity water is subjected to electrolysis thereby splitting the water to produce hydrogen. This is achieved by the incorporation of one or electrodes into the RO type semi-permeable membranes conventionally used in these pressure-driven energy generation processes to provide modified membranes that allow simultaneous splitting of the water via electrolysis in addition to the standard PRO conventionally carried out process using these types of membrane.

Pressure retarded osmosis (PRO) is an osmotically driven membrane process that uses energy harnessed from the mixing between high and low salinity streams to produce mechanical energy (utilization of Gibb's free energy of mixing). Water permeates through RO type semi-permeable membranes from a low concentration feed stream into a high concentration, partially pressurized, brine stream ("draw solution"). The hydraulic pressure is less than its osmotic pressure resulting in a net osmotic driving force for transport of water (permeate stream) from the feed stream to the brine stream. The permeate stream becomes pressurised and dilutes the brine stream and the energy in the pressurised permeate stream can be converted into mechanical or electrical energy via a turbine generator.

Forward osmosis is an alternative osmotically driven membrane process that uses the RO type membrane to treat two liquid feed streams. One side of the membrane is a feed solution (FS) with a low osmotic pressure and the other side of the membrane is the draw solution (DS) with a higher osmotic pressure. The difference in osmotic pressure causes water to pass through the membrane from the FS side to the DS side, simultaneously diluting the DS and concentrating the FS. The RO type membranes

consist of an active layer (or salt rejection layer) and a porous support layer, with the FS side generally facing the active layer.

Both these processes generate a very low salinity water stream across the membrane. The present invention utilizes this water stream for the production of hydrogen. However, the invention is not limited to these types of membrane and could also be implemented in other types, such as reverse osmosis membranes and nanofiltration membranes. A RO type semipermeable membrane is basically a very thin layer of polymeric material that acts as a barrier layer and separates dissolved ions or molecules from water when the applied pressure is greater than osmotic pressure.

In one embodiment, the present invention utilizes a permeate stream produced during PRO or FO. This stream cannot be directly measured because it cannot be extracted from the membrane and is extremely thin. However, the inventors have recognized for the first time that this stream may be used for hydrogen production due to its extremely low salinity. In this respect, it is not readily known that at the contact surface between the salt rejection layer and the support layer of FO and/or PRO membranes there is continuous movement of low salinity water which has salinity about 1000 times less than feed solution (seawater) moving on one side (FS) of the FO/PRO membrane and about 10,000 less salinity than the draw solution (DS) on the other side. The present innovation positions electrodes in this extremely thin low salinity stream for the purpose of water split for hydrogen and oxygen production. Thus, the present invention provides novel permeable membranes for enabling water split and furthermore, provides a novel method and system for generating hydrogen and oxygen from water.

The invention may also be incorporated into RO and NF processes wherein a small portion of the raw salinity feed water and/or permeate water is subjected to electrolysis thereby splitting the water to produce hydrogen. This is again achieved by the incorporation of one or electrodes into the RO type semi-permeable membranes conventionally used in these pressure-driven water desalination processes to provide modified membranes that allow simultaneous splitting of the water via electrolysis in addition to the standard water desalination conventionally carried out using RO type of membrane.

Alternatively, the invention may be incorporated into UF and MF processes wherein a small portion of the feed water and/or filtrated water is subjected to electrolysis thereby splitting the water to produce hydrogen. This is again achieved by the incorporation of one or electrodes into the UF type of membranes conventionally used in these pressure-driven water treatment processes to provide modified membranes that allow simultaneous splitting of the water via electrolysis in addition to the standard water treatment conventionally carried out using UF types of membrane.

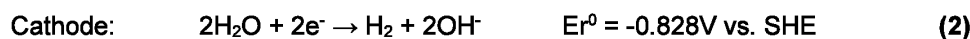
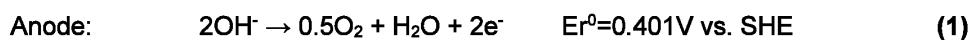
The following explanation applies equally to RO; NF; PRO; UF; MF processes that be modified according to the invention to provide hydrogen generation.

The invention provides for simultaneous water desalination (RO, NF) or water treatment (UF, MF, FO) or osmotic power generation (PRO) and electrochemical production of hydrogen gas for conversion and storage of electrical energy (hydrogen economy). Electrochemical and membrane reactors have at least two common components: spacers and membranes. Moreover, modern water electrolysis systems utilize ultra-pure water. Electrolysis of deionized water directly in a desalination or filtration module using same membranes, spacers, control and automation units, hydraulic system, and other equipment and materials will reduce drastically operational and capital costs of water electrolysis and will provide an added value to the desalination or water treatment plants.

Conventional water electrolysis processes are operated at current densities of 200 to 2000 mA/cm² (and even higher). These high current densities are required to decrease the footprint of reactors and to minimize capital costs of these processes. There are currently three main processes for hydrogen production using water electrolysis (WE): (i) alkaline water electrolysis (see Figure 1A), (ii) polymer electrolyte membrane (PEM) electrolysis (see Figure 1B); and (iii) steam or solid oxide electrolysis (SOE). The SOE processes are performed at high temperatures (>500°C) and are not relevant to the present invention and thus will not be discussed in any further detail.

All WE techniques are based on oxidation and reduction of water molecules or H⁺ and OH⁻ ions into oxygen and hydrogen gases on anodes and cathodes. These processes consume electrical energy and heat with the reaction occurring at the anodes and cathodes being dependent upon the pH in the electrolyzed solution, as set out below:

In alkaline solutions (See Fig. 1A):



In acidic solutions (See Fig. 1B):



(where V_{rev} is a reversible voltage (Volt), E^0 is a standard reduction potential (Volts vs. standard hydrogen electrode, SHE).

The oxidation and reduction processes proceed on the anodes and cathodes, respectively. In all electrolysis cells, the anodes are more positive than the cathodes. The electrons flow from anodes to cathodes (i.e., in the direction opposite to a flow of electric current) through an external wire (or other, normally metallic conductors) connected to a direct current (DC) supply. The electrical circuit of the electrochemical cell requires movement of electrical charges (i.e., ions) in the electrolyzed solution. In other words, an electrolyte must be present in water to sustain the WE process. Two major types of electrolytes are used in low temperature (i.e., $T \leq 100^\circ\text{C}$) water electrolysis processes: (1) salts, acids, and bases; and (2) solid electrolytes.

As follows from Eqs (1)-(4) above, anodic and cathodic reactions produce H^+ and OH^- ions in the electrolyzed solution. These ions can be utilized to conduct the ionic current in water electrolysis. In this case no addition of external electrolyte would be required. This principle is utilized in solid electrolyte water electrolysis processes, as shown in Figure 1B. The “solid electrolyte” term refers to an ion-exchange membrane which is located between anode and cathode in an electrochemical cell. Normally polymeric cation-exchange membranes (e.g., Nafion, the sulphonated tetrafluoroethylene-based fluoropolymer-copolymer) are used in this type of WE devices. For this reason, the term “proton exchange membrane (PEM) water electrolysis” and the abbreviation PEM are used in professional literature. The membrane in its original form contains fixed

negatively charged sulfonic groups and exchangeable H^+ ions. Anodic production of oxygen via reaction Eq. (3) results in generation of H^+ ions. These ions flow through the membrane (ionic current in a “solid” electrolyte) and get consumed within the hydrogen evolution reaction that proceeds on a cathode via reaction Eq. (4). This way the overall concentration of H^+ ions in the membrane remains constant. The PEM electrolyzer requires ultra-pure deionized water (less than 0.5 ppm of total dissolved solids to prevent deterioration of membranes) and expensive noble metal catalysts (e.g., IrO_2 for anodes and Pt for cathodes).

These conventional water electrolysis processes require ionic carriers that can be (1) originally present in the electrolyzed water (e.g., seawater), (2) added into deionized water (e.g., alkaline water electrolysis), or (3) provided with the ion-exchange membranes. Electrolysis of pure water is not generally carried out.

Seawater is potentially an endless source of water for electrochemical generation of hydrogen. However, there are two crucial obstacles that must be overcome for the development of industry-scale hydrogen production by seawater electrolysis: (1) scaling of cathodes with Ca and Mg deposits, and (2) production of chlorine species by anodic oxidation of chloride ions.

With regard to the scaling issue, seawater contains significant amounts of magnesium and calcium ions that precipitate in alkaline solutions and/or on a cathode due to the high local pH that exists in the near cathode area because of hydrogen evolution reaction. The pH that develops in the near cathode area at current densities of $> 100 \text{ mA/cm}^2$ can be as high as $\text{pH}=12$. Consequently, the direct seawater electrolysis at current densities $\geq 200 \text{ mA/cm}^2$ inevitably results in detrimental deposition of Ca and Mg species on cathodes.

Furthermore, anodic production of chlorine gas also creates a significant problem. In this respect, seawater contains high concentrations of chloride ions that can be oxidized on an anode to produce chlorine gas. This is then hydrolyzed into hypochlorous acid (HOCl) which exists in equilibrium with hypochlorite ions (OCl^-). At Cl^- concentrations typical for seawater (ca. 20 g/L) current density for Cl_2 evolution reaction can be as high as $>70\%$. This means that Cl_2 is the primary anodic product if

direct seawater electrolysis process is performed using typical water electrolysis anodes (e.g., graphite, Pt, mixed metal oxides, IrO₂, etc.). Production of chlorine in seawater electrolysis aimed at mass production of H₂ must be prevented.

The present invention reduces or eliminates all these problems by the incorporation of electrodes into the conventional pressure-driven membranes utilized in desalination or water treatment processes. This represents a significant step forward in the generation of hydrogen from accessible water sources.

The processes and systems of the present invention which perform simultaneously pressure-driven membrane filtration of water with electrochemical splitting of water to produce hydrogen are very different to the prior art large scale electrochemical splitting of water. The present invention provides hydrogen production at ≈ 1 g/m²/h range corresponding to a current density of ≈ 3 mA/cm² which is extremely low if compared to electric currents applied in the state-of-the-art alkaline and solid electrolyte water electrolysis reactors (200-2000 mA/cm²). However, the integration of electrochemical process into the water desalination or filtration modules according to the present invention is not expected to result in a larger footprint of desalination or water treatment facilities already in existence. Moreover, operational costs are expected to be even lower than the well-established water electrolysis technologies. This is, for example, because electrolysis of seawater (or RO brine or other water to be purified) at very low current density (1) consumes less energy per unit volume of generated hydrogen gas; (2) does not produce chlorine, which is unwanted in seawater electrolysis aimed at hydrogen gas production; (3) can be performed using cheap catalysts with longer operational lifetime; and (4) will not produce detrimental precipitates of, for example Ca and Mg salts on the cathodes.

Usually desalinated water includes Ca, Mg, Na, CO₃, SO₄, HCO₃, Cl and other ions in an amount 10 to 300ppm. During water split the concentration of dissolved solids in permeate water stream is increasing. If all permeate is used for split, two problems will arise; (i) scaling formation CaCO₃, CaSO₄ etc and (ii) increased conductivity of permeate which will increase power consumption for hydrogen generation. The combination of two processes (desalination and split), (energy generation and split) or (water filtration and split) in one membrane element solves this contradiction.

Furthermore, the invention is cost efficient because common water pumping and water filtration equipment is used for the two combined processes.

Any pressure-driven membrane that provides for desalination or filtration of water may be adapted to simultaneously produce hydrogen according to the present invention, such as RO, NF, PRO, FO, UF and MF membranes. In the context of this disclosure, these are referred to as RO-type or UF-type membranes and generally these consist of semi-permeable membranes with a maximum pore size of 0.1 microns. In this respect, the type of membrane will have a particular pore size, for example MF membranes generally have a maximum pore size of about 0.1 microns; UF membranes generally have a pore size of 0.01 to 0.1 microns; NF membranes generally have a maximum pore size of 0.01 microns and RO membranes generally have a pore size of 0.0001 microns.

Figures 2A and 2B of the accompanying drawings illustrate one embodiment of a novel semi-permeable membrane 3 according to the present invention which may be incorporated into a PRO or FO module to carry out the process as described above. The membrane is provided with electrodes 9, 10 which enable it to be used for hydrogen generation in addition to its conventional use.

Referring to Figure 2A, a feed stream (saline solution, FS) 7 is delivered to a feed side 2 of the semipermeable membrane 3. The membrane 3 consists of a salt rejection layer 4 and support layer 5 with a series of parallel electrodes 9, 10 positioned between the salt rejection layer 4 and the support layer 5. During forward osmosis (FO) or pressure retarded osmosis (PRO), part of the feed stream 7 (saline solution) moves from the feed side 2 of semipermeable membrane through the salt rejection layer 4 (omitted from Figure 1B for sake of simplicity) and support layer 5 to the opposite side 1 (draw side) as permeate 8. This permeate stream 8 has a very low salinity (around 2%) and thus has an osmotic pressure lower than the feed stream 7 (PO_f) and lower than the draw solution stream 6 (PO_r).

Movement of stream 8 (permeate) takes place under balance of osmotic and gauge pressures PO_r; PO_f; PG_r; PG_f. This stream 8 (permeate), exists only as a moving stream during active FO or PRO process. It cannot be extracted as liquid but due to its very low salinity it can be electrochemically split during transit through the body of

semipermeable membrane 3. This is achieved by electrodes 9, 10 incorporated into the membrane 3 which allow a direct current to be applied to the permeate stream 8 causing the water to dissociate into hydrogen 11 and oxygen 12 which may then be collected for later use.

Figures 3, 4 and 5 of the accompanying drawings illustrate alternative embodiments of semi-permeable membranes 3 according to the present invention, the membranes 3 being provided with electrodes 9, 10 in different positions within the membrane. Identical features already discussed in relation to Figures 2A and 2B are given the same reference numerals.

Figure 3 shows the membrane 3 with both electrodes 9, 10 (anode and cathode) positioned externally on the surface of the salt rejection layer 4. In contrast, Figure 4 shows membrane 3 with both electrodes 9, 10 positioned between the support layer 5 and the salt rejection layer 4. In Figure 5, one electrode 10 is positioned between the support layer 5 and the salt rejection layer 4 with the other electrode 9 positioned on an external surface of the salt rejection layer 4.

Additionally, the semi-permeable membrane may comprise a module having a permeate tube and flat membrane sheets wound around the tube to provide a membrane element and incorporating permeate and/or feed spacers (supporting layers between the membrane sheets). These types of membrane elements or modules may also be adapted to incorporate electrodes in accordance with the present invention. Figure 6A shows a fragment of such a membrane 3 arrangement. It is single fragment of RO membrane with raw feed flow 42 and permeate flow 43. Support layer 5 and salt rejection layer 4 forms entire membrane 3.

A permeate spacer 41 is provided on the support layer side 5 of membrane 3 and a feed spacer 40 is provided on the salt rejection side 4 of membrane 3. This is a typical arrangement presented in Fig-6A. However, it is to be appreciated that other arrangements may be provided, such as positioning salt rejection layer 4 facing permeate spacer 41. Electrodes 9 and 10 are positioned on opposite sides of permeate spacer 41. In another embodiment, electrodes may be positioned on the same side (not shown). In other embodiments, three and more electrodes may be positioned on the same side or on both sides of permeate spacer 41 (again not shown).

In other embodiments, one, two, three and more electrodes may be positioned on the same side or on both sides of the permeate spacer 41 and/or on feed spacer 40 (not shown). This arrangement of electrodes positioned on feed spacer 40 and/or permeate spacer 41, may be combined with electrodes positioned on salt rejection layer 4 and support layers 5 of membrane 3 as described above. The position of the salt rejection layer in some membranes may be orientated to permeate channel instead of feed channel (again this is not shown in the accompanying figures).

Thus, the electrodes 9, 10 may be incorporated into multiple types of filtration membranes and are not limited to those shown and described herein. This includes membranes that may consist entirely of a salt rejection layer 4 and do not have support layer 5 and/or feed or permeate spacers.

Figure 6B shows a fragment of two membranes 3 arranged in mirror symmetry in RO module with arrows for the raw feed flow 42 and arrows for the permeate flow 43 passing between membranes 3. Permeate flow generated on the membrane 3 is shown as arrow 44, which joins permeate flow 43 coming from other membranes positioned in the module. This represents a typical mirror RO membranes arrangement format where the raw saline solution feed channel 42 includes feed spacer 40 and permeate channel 43 has permeate spacer 41 positioned in it.

Thus, it is to be appreciated that any type, number and arrangement of electrodes may be provided within the membrane to allow water splitting to be carried out. Two or multiple electrodes may be installed between salt rejection and support layers, the electrodes can be installed in the support layer only, in rejection layer only or the electrodes can be installed in both layers.

The electrodes must have the necessary conductivity and one of the electrodes may comprise the active or salt rejection layer 4. A preferred embodiment of the semi-permeable membrane has a salt rejection layer that also forms one of the electrodes. One preferred material for the electrode, which may also comprise the active or salt rejection layer 4, is graphene. However, another suitable material is titanium. The substrate for the electrode may, for example, comprise a mesh, plate, cloth formed of fiber or a sintered body. Dielectric layers may also be incorporated into the

membranes between the electrodes. The layers may be interconnected and may be produced by techniques such as casting or printing, gluing or growing.

The electrode (anode and/or cathode) may also be at least partially coated with at least one catalyst, such as one selected from the group consisting of iridium oxide, ruthenium oxide, tantalum oxide, titanium oxide, platinum, and platinum oxide, and any combination thereof.

In embodiments where the electrode comprises graphene or a carbon fiber/cloth, the carbon substrate is preferably coated with mixed metal oxides (MMO) selected from Pt, Ir, Pt-Ir and Ru metals and any combination thereof.

Preferably, the carbons are substrates for coating with mixed metal oxides (MMO) selected from platinum (Pt), iridium (Ir), Pt-Ir, ruthenium (Ru) metals and any combinations thereof. In these embodiments, the MMO/C electrodes may be prepared by a two-step process comprising forming a sacrificial copper or nickel layer on the carbon via electroless or electrodeposition and displacing the sacrificial metal by Pt, Ir, Ru or Pt-Ir.

The present application is equally suitable for two, three or more electrode systems, such as cathode, anode and reference electrodes, or other. Additional non salt rejection layers (membranes) can be installed near to the electrodes.

As is known in the art, feed spacers are used in spiral wound reverse osmosis membrane modules to keep the membrane sheets apart as well as to enhance mixing. They are beneficial to membrane performance but at the expense of additional pressure loss. The feed spacers are a netting material placed between the flat sheets of a reverse osmosis membrane to promote turbulence in the feed / concentrate stream. Usually, feed spacers are made of plastic polypropylene.

A permeate or channel spacer is also known as a "permeate water carrier", or "mesh spacer". In the construction of a membrane element, the permeate spacer is placed between two layers of the flat sheet membrane. This spacer is used to prevent the RO membrane from closing-off on itself under the high pressure of operation. Permeate water will flow in a spiral path across the product channel spacer into the product

collection tube. The permeate spacer is inside the envelope and creates a flow pass for permeate water. Additionally, it supports the membrane sheets mechanically against (high) feed pressure and therefore it is made of woven spacers with low permeability to have the required stiffness. Usually, permeate or channel spacers are made of woven thin plastic (e.g., a knit fabric called Tricot).

It is to be appreciated that the electrode (anode and/or cathode) may also comprise the feed or permeate spacer as discussed above, for example wherein the spacer is at least partially coated with an electrically conductive layer to make the spacer electrically conductive and/or a catalytic layer to make them electrocatalytically active as anodes (O₂ evolution) or cathodes (H₂ evolution) or both. The catalyst may be for example Pt, Ir, Ni, Cu metals or any combination thereof.

Alternatively, the electrode (either anode or cathode) may be coupled to the permeate or feed spacer, which is in mechanical co-operation with the permeate tube. An example of such an embodiment is shown in Figure 10 of the accompanying drawings wherein two electrodes 402 are coupled to spacers attached at one end to a permeate tube 400. Any number of electrodes and spacers may be provided, as shown in Figure 11 which has 20 electrodes 402, coupled to spacers, which are coupled at one end to the permeate tube 400.

According to another embodiment of the present invention, Titanium foil cladding to permeate and/or feed spacers with and without additional electricity conductors between titanium foil and plastic spacer.

Thus, the electrode is essentially the Titanium foil cladding.

Reference is now made to Figure 12 illustrating a Titanium foil cladding 300 to permeate and/or feed spacers with and without additional electricity conductors between titanium foil and plastic spacer.

In the example illustrated in Figure 12, the Titanium foil 300 is cladded to the permeate spacer 41. However as specified above, such cladding could be performed to the feed spacer 40 as well.

According to one embodiment, the cladding is performed on one side of the permeate and/or feed spacers. According to another embodiment, such cladding is performed on both sides of the permeate and/or feed spacers.

According to one embodiment, the cladding may be done by application of vacuum. According to such an embodiment, on one side of the permeate and/or feed spacers the foil is positioned and on the other side vacuum is applied. Such suction will adhere the Titanium foil 300 to the permeate and/or feed spacers.

The thickness of such Titanium foil 300 can be varied and depending of the electrical conductivity needed.

According to another embodiment, in addition to the Titanium foil cladding 300, electrical wires can be added to enable the electrical current transfer. Such is also seen in Figure 12. Thus, as seen in Figure 12, according to some embodiment, electrical wires 301 are also added to the permeate spacer 41.

The method of water split carried out within the membrane can be conducted using any one of the conventional techniques for water electrolysis, such as water electrolysis (WE), PEM Electrolysis, Microbial Electrolysis, Solid Oxide Electrolysis, Alkaline Electrolysis, or any other way of water split. Thus, the invention is not limited to one particular process of water split.

Different types of hydrogen and oxygen evacuation systems (not shown on drawings) may be applied to remove the gases from the membrane system. Preferably, hydrogen and oxygen are evacuated from the membrane element or module together with the water stream in which they were generated. Extraction of hydrogen and oxygen may then take place in a degasifier. The solubility of hydrogen and oxygen in water is very different enabling extraction of hydrogen to take place in the degasifier at a pressure at which oxygen is still dissolved. Oxygen together with water stream may then go to next degasifier with a lower gauge pressure, where oxygen may then be extracted. Alternative, a gas separation membrane may be utilised.

The present invention allows low salinity water produced during treatment of water, such as seawater, brine and brackish water to be electrochemically split to provide hydrogen in addition to the treated water.

In an embodiment utilising RO-type membranes for desalination of feed water, one RO module may be provided with several membrane elements and feed seawater is concentrated as it moves from one membrane to the next membrane element in the module. For example, the first element in a module may have seawater 3.5% TDS and

in the 8th membrane element 8% TDS. The water electrolysis will be different in different membrane elements having different salinity. The electrical system may be adjusted to provide different electrical current (voltage) to different membrane in module.

Conventionally, one RO module contains 5-8 membrane elements. It may be desirable to install the electrodes for water split on only the few first elements in the pressure vessel where permeate has less or more dissolved solids, and electrical conductivity is less or more which increases efficiency for split.

Preferably, only part, at most 5% (but preferably less than 2.5%), of the desalinated permeate stream produced during the RO process is split into hydrogen and oxygen. This provides an important technological benefit in that permeate is never free from dissolved suspended solids.

Figure 7 of the accompanying drawings illustrates a conventional seawater desalination plant that may be adapted to include membranes with electrodes to provide a dual water desalination and hydrogen generation plant. In brief, sea water SW is delivered, via intake channel 101, through various pre-treatment sites 102, 103, 104, 105 before being pumped under pressure by virtue of pumps 108 through multiple reverse osmosis passes 110, 112 to form desalinated product water 114 and concentrated sea water or brine 116. The product water may be subjected to post-treatments 118 and held in a holding tank 120, while the brine 116 is discharged back into the sea via a discharge channel 122.

The reverse osmosis passes 110, 112 are each made up of multiple membrane elements 201, one of which is exemplified and expanded in Figure 8. A central perforated product tube 202 extends through the centre of each element and is surrounded by sheets of semi-permeable membrane 204 wound around the tube and separated therefrom by a feed spacer sheet 206 and a permeate spacer sheet 208. An anti-telescoping cap 210 is provided at each end. As discussed above, a raw saline feed solution is fed into one end of the element 201 to provide permeate stream 114 and residual brine stream 116 with a permeate flow PF through the layers of the element. Electrodes (not shown) can be incorporated within the element to allow electrochemical splitting of raw saline solution and/or permeate to create a smaller

output of hydrogen generation (not shown) together with a main output of residual brine stream 116 and/or permeate product water 114.

The process and system for simultaneous water treatment and electrochemical splitting of water according to the present invention addresses many problems associated with prior art generation of hydrogen from seawater and other water sources.

For example, the possibility of cathodic precipitation of CaCO_3 , Ca(OH)_2 , Mg(OH)_2 and other species in the hybrid reactors proposed by the Applicant for simultaneous water treatment and H_2 production is significantly lower due to (i) very low current density, (ii) very high water flux, and (iii) the pH buffering capacity of seawater (relevant only if cathodes are located in feed and/or in concentrate compartments).

Furthermore, the chlorine evolution reaction in seawater electrolysis can be depressed due to the very small anodic current density of $\approx 1 \text{ mA/cm}^2$.

This is illustrated in Figure 8 of the accompanying drawings which is a graph showing reversible potentials for chlorine evolution, oxygen evolution and hydrogen evolution reactions as a function of pH. $T = 25^\circ\text{C}$, $[\text{Cl}^-] = 20 \text{ g/L}$ fugacity of gases =1, no complexation, infinite dilution. This shows the values of reversible potentials (vs. SHE) for oxygen evolution (Eq.(3) *supra*) chlorine evolution (Eq. (6) *supra*), and hydrogen evolution (Eq.(4) *supra*) as a function of pH at conditions typical for seawater electrolysis (i.e., $[\text{Cl}^-] = 20 \text{ g/L}$, fugacity of gases =1, no effect of complexation, infinite dilution). In WE the electrode potential for anodic reactions must be higher than the reversible potential. For cathodic H_2 production the cathode potential must be lower than the reversible potential of this reaction. As it is show in Figure 8, the minimal cell potential (i.e., difference between anode and cathode potentials) required for chlorine evolution in seawater ($\text{pH} \approx 8.1$) is 1.78 V. On the other hand, the minimal cell potential required for oxygen evolution on an anode and hydrogen evolution on a cathode is only 1.23 Volt. Consequently, there is a range of cell potentials at which only oxygen will be produced on the anode and hydrogen will be produced on a cathode. Normally, this maximal cell potential limits the anodic current density to the very low current density of only few mA/cm^2 . The current densities typical for alkaline water electrolysis is 200–400 mA/cm^2 , and 600–2000 mA/cm^2 for PEM water electrolysis and thus,

chlorine generation would be a problem. In contrast, the very small current density applied in the present invention allows chlorine generation to be depressed.

Furthermore, the proposed technique has the same thermodynamics as the conventional water electrolysis processes. Generally, operation at higher current density (i.e., larger production rates per reactor volume) requires higher energy input (or cell potential), while the energy/H₂ ratio increases at higher current densities. In other words, very low current densities that will be utilised for the process of the present invention is expected to result in lower electrical energy consumption for hydrogen production compared to the state-of-the-art technologies. The main reasons for this lower energy consumption are as follows: (1) lower activation overpotential is required to achieve lower current density, (2) very low diffusion and concentration overpotentials due to very effective mass transport in the proposed systems, (3) gas generation at no formation of bubbles. The last is due to a relatively low H₂ and O₂ production rates and very high flowrates of water that will result in complete dissolution of generated gases. Conventional water electrolysis systems cannot be operated at very low current densities because the footprint of the H₂ production system and construction costs would be unreasonably high.

In this respect, one of the main requirements to modern water electrolysis processes is low energy consumption at sufficient (i.e., > 200 mA/cm²) current densities. High current density is required to decrease the construction costs, the footprint, and amounts of expensive materials, such as catalysts, membranes, bipolar plates, etc. To put it simply: construction of large conventional water electrolyzer operated at very low current density is economically unfeasible due to very high construction costs that would diminish the benefits of low energy consumption.

However, the integration of a hydrogen-producing process in conventional water desalination/filtration systems according to the present invention is possible without any increase in their size or any significant decrease in water treatment performance. For example, permeate and feed spacers of RO, NF, UF, and FO modules, as well as membrane layers of NF, MF and UF membranes can be used as they currently are for separation of anodes and cathodes incorporated therein to provide the desired hydrogen generation. Consequently, the capital costs of the proposed H₂ production

systems are expected to be relatively low, as they utilize materials, water preconditioning systems, and other units that already exist in pressure-driven membrane filtration processes.

Another important potential advantage of low current density operation is a possibility to apply cheap catalysts. This is because the rate of catalyst's wear is normally faster at higher current densities. This is an important reason for utilization of noble metal catalysts in conventional PEM electrolyzers. To summarize: in spite of the fact that the proposed technologies will have to utilize larger amounts of materials (per unit volume of generated H₂), the attributed hydrogen costs are expected to be lower to the conventional WE process due to the longer service life and significantly lower price of the materials.

Conventional water electrolysis electrodes comprise the "real electrode" which is a very thin ($\approx$ few microns) layer of catalysts, and secondary layers, such as a gas diffusion layer (GDL). The GDL is used to achieve fast mass transport of gaseous products from the electrode, and to drive electrons to (or from) the electrode. The GDLs of modern PEM water electrolyzers contain hydrophobic particles for fast transport of gaseous species. Next to the GDL the current collector is used to provide a flow of electrons to (or from) the GDL and the catalyst layer. The current collectors have flow-fields to distribute water on the electrode surface and to collect the produced gases. The thickness of current collectors is normally ≥ 3 mm and they are made of highly conductive material (e.g., graphite, composite of polymer and conductive particles, or metals).

In contrast, the electrodes of the electrolysis cells proposed by the semi-permeable membranes of the Applicant must be made of conducting fibers which are relatively long (i.e., up to 100 cm inside the membrane) and relatively thin (apparently up to 100 μ m). This geometry would be barely possible in conventional WE operated at high current density. This is due to a high resistance of fiber-type electrodes. However, a simple calculation shows that this fiber type geometry is applicable in the systems and processes proposed herein:

Assumptions: thickness of the electrode = 100 μ m, area of the membrane = 100·100 cm·cm, fraction of cross-section occupied by electrodes = 50%, current density = 3 mA/cm², effective electrolysis area is equal to membrane area.

Considering the parameters assumed above the cross-sectional current density (the ratio between current and cross-section of fiber electrodes) becomes $\approx 0.6 \text{ A/mm}^2$. This means that if the electrodes have electrical conductivity of $1.27 \cdot 10^5 \text{ (S/m)}$ (typical for graphite in basal plane) the ohmic voltage drop in 100 cm long electrode at a current of 30 A will be only $\approx 50 \text{ mV}$. This simple calculation shows that the proposed electrochemical cells are feasible if fiber type electrodes are made of material with high electrical conductivity (i.e., within a range of stainless steel or titanium).

Figure 9 of the accompanying drawings illustrate one scheme which may incorporate the system for generating hydrogen as hereinbefore described. In particular, the scheme allows for production of green energy using osmotic power generation from salt domes, the energy then being utilised for water split as hereinbefore described followed by storage of the hydrogen in empty salt caverns. In this manner, the invention provides an extremely energy efficient manner for the production of green energy in the form of hydrogen.

The scheme involves 3 cycles; cycle 100 involving efficient energy generation by PRO using the different salt concentrations between sea water 2 and dissolved salt water from salt domes 26; cycle 200 involving hydrogen generation from water electrolysis using the electricity produced in cycle 100 and cycle 300 which evacuates the hydrogen produced in cycle 200 and delivers it for storage in salt dome caverns 35 formed during salt extraction for the PRO in cycle 100.

In further detail, cycle 100 creates electricity using Pressure Retarded Osmosis process (PRO). The PRO is driven by the difference in salinity between highly concentrated salt 10-25% (draw solution DS) dissolved from salt domes 26 and seawater 3.6-4.5% (the feed solution FS). The dissolution of salt rock in salt caverns 26 as an option can take place under high gas pressure PGr which can be of about 200 bar and forms the draw solution. Alternatively, the dissolution can take place under atmospheric pressure. This draw solution is delivered to a first PRO module 100 by means of pump 25 via pipe line 23 and enters the first side of the module 100 via inlet 22 the first side. The feed stream (FS) enters the second side of the PRO module 100 via inlet 20. Part of the feed stream penetrates from the second side to the first side of the membrane 3 as low salinity permeate and mixes with the draw solution. A

mix of the draw solution and permeate then exit module 100 via outlet 23. Part of this mix is directed to turbine 27 for electricity generation.

The residual amount of the feed stream is discharged from module 100 via outlet 21 to environment (for example, the sea as shown in Figure 5)

The electricity generated in turbine 27 or similar device from the output from module 100 is then directed to a Forward Osmosis (FO) module 200 as energy source for electrochemical water split into hydrogen and oxygen, with the low salinity water for water split coming from FO process and the water split being achieved by the incorporation of a membrane according to the invention into the module that has electrodes for effecting electrolysis. Sea water 2 may be used for the feed solution 30.

Module 200 FO from construction point of view is similar to PRO module 100. Movement of permeate stream from the feed side of membrane to the draw side also takes place under balance of osmotic and gauge pressures PO_r ; PO_f ; PGr ; PGf . However, the difference between modules 100 and 200 is in the gauge pressures PGr ; PGf . On module 200 the PGr and PGf are low and permeate movement from the FS side to the DS side takes place mostly under the difference in osmotic pressures PO_r and PO_f . The membrane has electrodes (i.e. 9,10 in Figures 1A to 4) and optionally an additional reference electrode (not shown in drawings). These electrodes, together with the electricity from module 100, allow splitting of the low salinity permeate stream to take place producing hydrogen and oxygen. Any residual water 33 may be returned to the sea 2.

It is to be appreciated that the semi-permeable membranes incorporating electrodes according to the present invention may be installed in module 100 and module 200, thus allowing water split to take place on module 100 and module 200 at the same time. Alternatively, the electrodes can be installed in module 100 only or in module 200 only.

Following production of hydrogen in cycle 200, the hydrogen is then stored in salt dome caverns 35 produced during salt extraction for PRO process 100.

The integration of electrochemical hydrogen production in RO membrane or UF/MF filtration processes provides significant and surprising benefits over prior art electrochemical treatment of water. The combination of water treatment and hydrogen production processes in one module is expected to significantly decrease operational and capital costs of hydrogen gas production, and to create an added value to water treatment facilities. The proposed technologies are expected to have significantly lower energy consumption than conventional water electrolysis techniques. The hybrid processes can be operated using cheap catalysts with very long operational life. These novel and inventive systems and methods according to the present invention perform simultaneously pressure-driven membrane filtration of water (e.g., reverse osmosis, forward osmosis, nanofiltration, ultrafiltration) and electrochemical splitting of water using the same hybrid reactors.

It is to be appreciated that modifications to the aforementioned membrane, process and systems may be made without departing from the principles embodied in the examples described and illustrated herein.

CLAIMS:

1. A membrane element configured for filtration of water while co-generating hydrogen, wherein the membrane comprising at least one anode electrode and at least one cathode electrode, each is in communication with said membrane; further wherein said membrane is adapted for electrolysis of at least a portion of said water to at least partially generate hydrogen therefrom.
2. The membrane element according to claim 1, wherein said membrane configured for filtration of water when a pressure difference is provided across said membrane.
3. The membrane element according to claim 1, wherein said membrane is configured for osmotic and/or gauge pressure driven filtration of water.
4. The membrane element according to claim 1, wherein said membrane is selectively permeable membrane configured to at least partially purify feed water when a pressure difference is provided across said membrane.
5. The membrane element according to claim 1, wherein at least one selected from a group consisting of said at least one anode electrode, said at least one cathode electrode and any combination thereof is made of at least one material selected from titanium, carbon fiber, carbon cloth, graphene and any combination thereof.
6. The membrane element according to claim 1, wherein at least one selected from a group consisting of said at least one anode electrode, said at least one cathode electrode and any combination thereof is at least partially coated or at least partially cladded with at least one catalyst.
7. The membrane element according to claim 6, wherein said catalyst is selected from a group consisting of iridium oxide, ruthenium oxide, tantalum oxide, titanium oxide, platinum, and platinum oxide and any combination thereof.
8. The membrane element according to claim 1, wherein at least one selected from a group consisting of said at least one anode electrode, said at least one cathode electrode and any combination thereof is provided in the form of at least one selected from a group consisting of mesh, plate, cloth, fiber, sintered body and any combination thereof.
9. The membrane element according to any one of claims 1-8, wherein the membrane comprises a salt rejection layer and a support layer, the at least one anode electrode and/or at least one cathode electrode comprising the salt rejection layer

- and/or being provided in, on or between one or both the salt rejection and support layers.
10. The membrane element according to any one of claims 1-9, wherein the membrane element includes at least one selected from a group consisting of feed spacers, permeate spacers and any combination thereof; and the at least one anode electrode and/or the at least one cathode electrode are provided by the feed or permeate spacer or are provided on or adjacent one or other of the feed and/or permeate spacers or are coupled to at least one selected from a group consisting of feed spacers, permeate spacers or are at least partially coated or at least partially clad on at least one selected from a group consisting of feed spacers, permeate spacers and any combination thereof.
 11. The membrane element according to any one of claims 1-10, wherein at least one electrode is formed from graphene.
 12. The membrane element according to any one of claims 1-11, wherein at least one electrode is provided in the form of a grid or parallel spaced apart strips.
 13. The membrane element according to claim 12, wherein at least one electrode is in the form of a full or partial coating or a full or partial cladding of the permeate and/or feed spacer.
 14. The membrane element according to any one of claims 1-13, wherein a catalyst is provided on one or both of the anode electrode and the cathode electrode.
 15. The membrane element according to any one of claims 1-14, further comprising collecting means for collecting the dissolved hydrogen in the product water or optional reject flow for subsequent extraction by degasification or gas membrane separation.
 16. The membrane element according to any one of claims 1-15, wherein the water filtration process is selected from the group consisting of reverse osmosis, pressure retarded osmosis (PRO), forward osmosis (FO), ultrafiltration, microfiltration and nanofiltration.
 17. The membrane element according to any one of claims 1-15, wherein a low current density below 100 mA/cm^2 is applied across the electrodes to enable electrochemical splitting of the water to occur, preferably being below 10 mA/cm^2 ; especially below 5 mA/cm^2 , ideally below 1 mA/cm^2 .
 18. A method of generating hydrogen during pressure driven water desalination process, comprising steps of:

a. supplying feed water to at least one membrane, comprising at least one anode electrode and at least one cathode electrode, in communication with said membrane;

b. filtering said water; while co-generating hydrogen;

wherein said step of co-generating hydrogen comprising step of applying either a potential difference or current between said at least one anode electrode and said at least one cathode electrode; thereby

generating by electrolysis hydrogen and oxygen from at least a portion of at least one selected from a group consisting of the feed, product water and any combination thereof.

19. The method according to claim 18, wherein said step of filtering said water additionally comprising step of applying a pressure differential across said membrane to draw feed water through said membrane to form a product water.
20. The method according to claim 18, wherein at least one selected from a group consisting of said at least one anode electrode, said at least one cathode electrode and any combination thereof is made of at least one material selected from titanium, carbon fiber, carbon cloth, graphene, and any combination thereof.
21. The method according to claim 18, wherein at least one selected from a group consisting of said at least one anode electrode, said at least one cathode electrode and any combination thereof is at least partially coated or at least partially clad with at least one catalyst.
22. The method according to claim 18, wherein said catalyst is selected from a group consisting of iridium oxide, ruthenium oxide, tantalum oxide, titanium oxide, platinum, and platinum oxide and any combination thereof.
23. The method according to claim 18, wherein at least one selected from a group consisting of said at least one anode electrode, said at least one cathode electrode and any combination thereof is provided in the form of at least one selected from a group consisting of mesh, plate, cloth, fiber, sintered body and any combination thereof.
24. The method according to any one of claims 18-23, further comprising collecting the dissolved hydrogen in the product water or optional reject flow for subsequent extraction by degasification or gas membrane separation.
25. The method according to any one of claims 18-24, wherein the water filtration process is selected from the group consisting of reverse osmosis, pressure

- retarded osmosis (PRO), forward osmosis (FO), ultrafiltration, microfiltration and nanofiltration.
26. The method according to any one of claims 18-25, wherein a low current density below 100 mA/cm^2 is applied across the electrodes to enable electrochemical splitting of the water to occur, preferably being below 10 mA/cm^2 ; especially below 5 mA/cm^2 , ideally below 1 mA/cm^2 .
27. A water filtration module configured for pressure driven filtration of water and electrochemical splitting of at least a proportion of the water for the co-generation of hydrogen, the module comprising:
- a feed water inlet;
 - at least one membrane element as claimed in any one of claims 1-17;
 - a product water outlet; and
 - optionally a reject water outlet.
28. The module according to claim 27, wherein the membrane comprises a salt rejection layer and a support layer, the at least one anode electrode and/or at least one cathode electrode comprising the salt rejection layer and/or being provided in, on or between one or both the salt rejection and support layers.
29. The module according to any one of claims 27-28, wherein the membrane element includes at least one selected from a group consisting of feed spacers, permeate spacers and any combination thereof; and the at least one anode electrode and/or the at least one cathode electrode are provided by the feed or permeate spacer or are provided on or adjacent one or other of the feed and/or permeate spacers or are coupled to at least one selected from a group consisting of feed spacers, permeate spacers or are at least partially coated or are at least partially cladded on at least one selected from a group consisting of feed spacers, permeate spacers and any combination thereof.
30. The module according to any one of claims 27-29, wherein at least one electrode is formed from graphene.

31. The module according to any one of claims 27-30, wherein at least one electrode is provided in the form of a grid or parallel spaced apart strips.
32. The module according to claim 29, wherein at least one electrode is in the form of a full or partial coating or a full or partial cladding of the permeate and/or feed spacer.
33. The module according to any one of claims 27-32, wherein a catalyst is provided on one or both of the anode electrode and the cathode electrode.
34. The module according to any one of claims 27-33, further comprising collecting means for collecting the dissolved hydrogen in the product water or optional reject flow for subsequent extraction by degasification or gas membrane separation.
35. The module according to any one of claims 27-34, wherein the water filtration process is selected from the group consisting of reverse osmosis, pressure retarded osmosis (PRO), forward osmosis (FO), ultrafiltration, microfiltration and nanofiltration.
36. The module according to any one of claims 27-35, wherein a low current density below 100 mA/cm^2 is applied across the electrodes to enable electrochemical splitting of the water to occur, preferably being below 10 mA/cm^2 ; especially below 5 mA/cm^2 , ideally below 1 mA/cm^2 .
37. A system for pressure-driven water purification with the co-generation of hydrogen, the system comprising:
- a feed water inlet;
 - at least one membrane element according to any one of claims 1-17 or module according to any one of claims 27-36;
 - at least one pump to apply a pressure to the feed water;
 - a power source to provide a potential difference to the electrodes of the membrane element;
 - a product water outlet; and optionally a reject flow outlet; and,
 - a hydrogen outlet within the product and/or reject flow.
38. A process for pressure driven water purification with co-generation of hydrogen, the process comprising:
- supplying feed water from a feed water inlet to a membrane element according to any one of claims 1-17 or module according to any one of claims 27-36;

- applying a pressure differential across the selectively permeable membrane of the membrane element to draw feed water through the membrane to form a product water and optionally a reject flow;
- applying a potential difference between the electrodes of the membrane element to cause electrochemical splitting of at least a portion of at least one of the feed and/or product water for form hydrogen and oxygen; and
- collecting the product water and optionally a reject flow, and hydrogen.
39. The process according to claim 38, further comprising collecting dissolved hydrogen in the product water or optional reject flow for subsequent extraction by degasification or gas membrane separation.
40. The process according to any one of claims 38-39, wherein the pressure driven water filtration process is selected from the group consisting of reverse osmosis, pressure retarded osmosis (PRO), forward osmosis (FO), ultrafiltration, microfiltration and nanofiltration.
41. The process according to any one of claims 38-40, wherein less than 5% of the feed and/or product water is split to form hydrogen, preferably the less than 1 %; more preferably less than 0.05%, especially 0.01%, ideally less than 0.01%.
42. The process according to any one of claims 38-41, wherein a low current density below 100 mA/cm^2 is applied across the electrodes to enable electrochemical splitting of the water to occur, preferably being below 10 mA/cm^2 ; especially below 5 mA/cm^2 , ideally below 1 mA/cm^2 .
43. The process according to any one of claims 38-42, further comprising delivering feed and draw solutions of different osmotic and gauge pressures to opposing sides of the selectively permeable membrane element; applying a current across the electrodes of the membrane to split the low salinity solution into hydrogen and oxygen; and collecting the hydrogen and oxygen.

44. The process according to claim 43, wherein the membrane is a RO-type membrane having a first side and a second side opposite the first side;

a first saline solution comprising the draw solution having an osmotic pressure P_{Or} and a gauge pressure P_{Gr} for entering the first side of the membrane;

a second saline solution comprising the feed solution having an osmotic pressure P_{Op} and a gauge pressure P_{Gp} for entering the second side of the membrane;

at least part of the feed solution from the second side of the membrane penetrating to the first side according to a net driving pressure defined by the balance of pressures P_{Gr} , P_{Or} , P_{Op} and P_{Gp} ;

wherein the draw solution and the penetrated part of the feed solution exit as a residual brine stream from the first side of the membrane via a residual brine outlet;

a remainder of the feed solution at least periodically exits as a residual fluid stream from the second side of the membrane via an outlet;

and

wherein at least a portion of a low salinity solution stream passes from the second side to the first side for splitting into hydrogen and oxygen as it passes across the membrane.

45. The process according to claim 43, wherein the membrane is a RO-type membrane having a first side and a second side opposite the first side;

a first saline solution comprising the draw solution having an osmotic pressure P_{Or} and a gauge pressure P_{Gr} for entering the first side of the membrane;

a second saline solution comprising the feed solution having an osmotic pressure P_{Op} and a gauge pressure P_{Gp} for entering the second side of the membrane;

at least part of the feed solution from the second side of the membrane penetrating to the first side according to a net driving pressure defined by the balance of pressures P_{Gr} , P_{Or} , P_{Op} and P_{Gp} ;

wherein the draw solution and the penetrated part of the feed solution exit as a residual brine stream from the first side of the membrane via a residual brine outlet;

a remainder of the feed solution at least periodically exits as a residual fluid stream from the second side of the membrane via an outlet;

and

wherein at least a portion of the first saline solution and/or the second feed solution is electrochemically split into hydrogen and oxygen as it passes along the membrane.

46. The process according to any one of claims 38-45, further comprising generating electricity using pressure retarded osmosis wherein the draw solution is provided by dissolving rock salt in salt domes.
47. The osmotic process according to claim 46, wherein dissolution of rock salt is carried out under pressure equal or near to PGr.
48. The osmotic process according to any one of claims 38-47, further comprising storing the generated hydrogen in the salt domes.
49. A system according to claim 38, for the production of hydrogen and oxygen from water further comprising an enclosure having at least one RO type membrane having at least two electrodes comprising a cathode and an anode, the membrane having a first side and a second side opposite the first side; an inlet for delivering a first saline solution comprising the draw solution having an osmotic pressure POr and a gauge pressure PGr for entering the first side of the membrane; a second inlet for delivering a second saline solution comprising the feed solution having an osmotic pressure POp and a gauge pressure PGp for entering the second side of the membrane; at least part of the feed solution from the second side of the membrane penetrating to the first side according to a net driving pressure defined by the balance of pressures PGr, POr, POp and PGp; wherein the draw solution and the penetrated part of the feed solution exit as a residual brine stream from the first side of the membrane via a residual brine outlet; a remainder of the feed

- solution at least periodically exits as a residual fluid stream from the second side of the membrane via an outlet and wherein a low salinity solution stream forms and passes from the second side to the first side; wherein the electrodes of the membrane serve to split at least a portion of the low salinity solution stream into hydrogen and oxygen as it passes across the RO type membrane.
50. A system according to claim 38, for the production of hydrogen and oxygen from water further comprising an enclosure having at least one RO type membrane having at least two electrodes comprising a cathode and an anode, the membrane having a first side and a second side opposite the first side; an inlet for delivering a first saline solution comprising the draw solution having an osmotic pressure P_{Or} and a gauge pressure P_{Gr} for entering the first side of the membrane; a second inlet for delivering a second saline solution comprising the feed solution having an osmotic pressure P_{Op} and a gauge pressure P_{Gp} for entering the second side of the membrane; at least part of the feed solution from the second side of the membrane penetrating to the first side according to a net driving pressure defined by the balance of pressures P_{Gr} , P_{Or} , P_{Op} and P_{Gp} ; wherein the draw solution and the penetrated part of the feed solution exit as a residual brine stream from the first side of the membrane via a residual brine outlet; a remainder of the feed solution at least periodically exits as a residual fluid stream from the second side of the membrane via an outlet and wherein a low salinity solution stream forms and passes from the second side to the first side; wherein the electrodes of the membrane serve to split at least a portion of the first saline solution and/or the second saline solution into hydrogen and oxygen as it passes along the RO type membrane.