(54) **Title:** MEMBRANE-TYPE WATER ELECTROLYSIS DEVICE FOR THE PRODUCTION OF GASEOUS HYDROGEN OR OXYGEN AT A CONTROLLED HUMIDITY LEVEL

FIG. 10
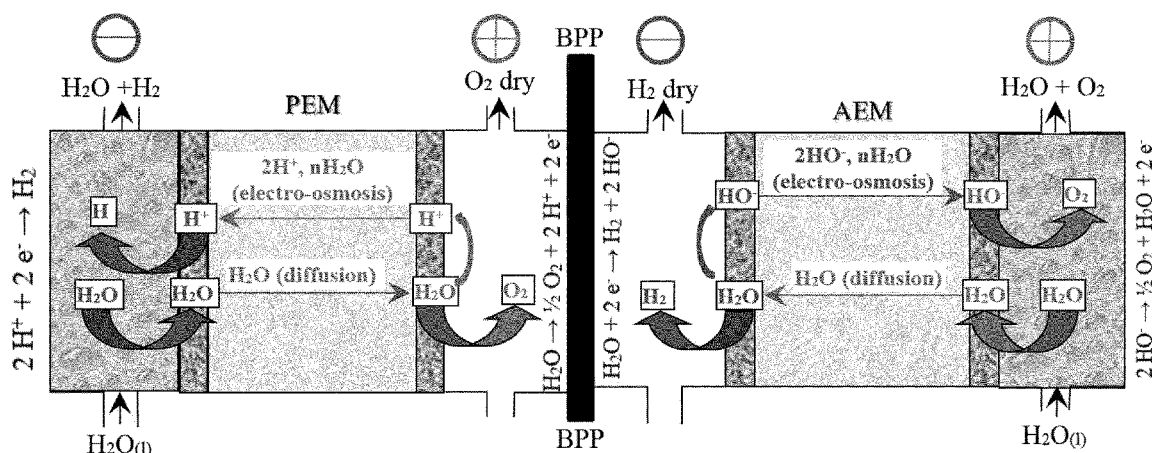
(57) **Abstract:** The present invention relates to a membrane-type water electrolysis device which can be used to produce gaseous hydrogen and oxygen at controlled humidity levels. This is achieved by using polymer electrolyte water electrolysis cells and simultaneously or separately adjusting two key operating parameters: the operating current density and the flow rate of water circulating in the water supply compartment which is placed on the side opposite to that where the water molecules are dissociated. To aid in the regulation of humidity levels, a hydrophilic water retaining additive can be added to the catalyst layer.

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

MEMBRANE-TYPE WATER ELECTROLYSIS DEVICE FOR THE PRODUCTION OF GASEOUS HYDROGEN OR OXYGEN AT A CONTROLLED HUMIDITY LEVEL

Technical field of the invention

5   The present invention relates water electrolysis device, and more specifically to a membrane-type water electrolysis device, for the production of gaseous hydrogen or oxygen at a controlled humidity level.

State of the art

10   Hydrogen is considered to be the energy vector of the future, enabling massive storage of renewable energy sources. In contrast to steam methane reforming, the dissociation of water by electrolysis allows the production of electrolytic quality hydrogen and oxygen, without any trace of carbon compounds. The apparatus that allows the dissociation of water into hydrogen and oxygen under the effect of an electric current is

15   an electrochemical reactor called water electrolyzer or, simply, electrolyzer. There are several technologies for water electrolysis, namely alkaline water electrolysis, polymer membrane electrolysis and ceramic membrane electrolysis.

Alkaline water electrolysis (AWE) operates between room temperature and typically 80°C and consists in the electrolysis of aqueous solutions of potassium hydroxide or

20   sodium hydroxide. The anodic and cathodic compartments are separated by a porous diaphragm, impregnated with electrolytic solution and permeable to the passage of electric current by ion transport.

Polymer membrane electrolysis (PEM = Proton Exchange Membrane or Polymer Electrolyte Membrane) operates between room temperature and typically 90°C and

25   consists in replacing the conventional liquid electrolyte with an ionic conduction membrane of the ionomer type. There are cationic conduction membranes (in water electrolysis, the protonic form is preferred; perfuorosulfonated polymer materials, PFSA = perfluorosulfonic acid, of the Nafion type are the most common ones) and anionic conduction membranes (in water electrolysis, the hydroxylic form is preferred; there are

30   several types of commercial polymers, e.g. Sustainion® or Flémion® mainly used in chlorine-soda electrolysis). Hyflon® type membranes (short-chain PFSA) can operate up to about 150°C; PBI type membranes doped with phosphoric acid can operate up to about 230°C.

A variant of the PEM technology is also known, which uses a membrane with ion-

2

selective conductivity by hydrated hydroxyls (OH-) ions. The technology is called AEM (Anion Exchange Membrane) or AEMWE (Anion Exchange Membrane Water electrolysis).

Ceramic membrane electrolysis typically operates between 600°C and 1000°C and uses a thin layer of solid inorganic material (e.g. doped alumina) with oxide ion conduction.

The present invention more specifically relates to polymer membrane electrochemical reactors. This type of reactor is well known and has many advantages such as good energy efficiency and great operating flexibility (flexibility, reactivity, cold start capability) with variable electrical load profiles, allowing it to be used for water electrolysis in combination with photovoltaic panels or wind turbines, or to provide various services to the electrical networks such as grid balancing or frequency regulation.

Figure 1 of the appended drawings is a cross-section view of a water electrolysis cell with polymer electrolyte membrane (C. Rozain, P. Millet, "*Electrochemical characterization of Polymer Electrolyte Membrane Water Electrolysis Cells*", Electrochimica Acta, 131 (2014) 160-167). With reference to Figure 1, the water electrolysis cell is generally indicated 10 and basically comprises an ion conduction membrane 1, with or without mechanical reinforcement, a cathodic catalytic layer 2 and an anodic catalytic layer 2', a cathodic porous layer 3 and an anodic porous layer 3', a cathodic porous spacer 4 and an anodic porous spacer 4' (e.g. metal grids), and two metallic bipolar plates 5 and 5'.

The assembly is usually mounted in a frame made of non-conductive technical polymer material equipped with distribution channels, a water injection and gas collection system, and seals (D. Bessarabov, P. Millet, PEM Water Electrolysis, "*Hydrogen and Fuel Cells Primers*", B.G. Pollet Editor, 1st Edition, Elsevier (2018)).

To fully understand the operation and limitations of a polymer electrolyte cell, be it a cationic one (PEM) or an anionic one (AEM), the flows of chemical species during electrolysis should be analyzed as a function of the electrode half reactions. In the current state of the art, hydrogen and oxygen leaving the membrane water electrolysis cells are saturated with water. Figure 2 shows the situation typically occurring in a PEM water electrolysis cell with wet anode and wet cathode, while Figure 3 shows the situation typically occurring in an AEM water electrolysis cell with wet anode and wet cathode.

3

Depending on the needs of downstream processes or users, the gases leaving the membrane water electrolysis cells are then more or less dried to meet the required standards. This results in additional costs in terms of capex (apparatus needed for drying) and opex (energy needed for drying).

5   The idea of feeding the catalytic layer, where the dissociation reaction of water molecules takes place, by diffusional transport of water through the polymer membrane from the opposite side has been proposed for the production of dry oxygen from a PEM water electrolysis cell. In this regard, Figure 4 shows a schematic diagram of a PEM water electrolysis cell with dry anode and wet cathode. The same idea has been used

10   for the production of dry hydrogen from an AEM water electrolysis cell. In this regard, Figure 5 shows a schematic diagram of an AEM water electrolysis cell with wet anode and dry cathode. Such a solution is disclosed in EP2451992B1.

However, this idea has several limitations. In practice, used as it is, the solution known from EP2451992B1 does not allow to produce dry hydrogen. Experience shows that

15   water vapour or even liquid water exits the membrane on the side where a dry gas is supposed to be produced. This solution does not allow to produce hydrogen or oxygen at controlled humidity levels either, because it is difficult to control the flow of water through the membrane. Furthermore, at high current densities, energy consumption becomes more important because additional energy must be provided to accelerate the

20   transport of water by diffusion; from an economic point of view, this nullifies the positive effect of dry gas production.

Many applications require hydrogen or oxygen with a controlled hygrometric degree (humidity level), i.e. with a water vapour content between 0% (i.e. dry gas) and 100% (i.e. gas saturated with water vapour at operating temperature T and operating

25   pressure p). An example is the production of medical oxygen. Another example is the production of hydrogen and oxygen for feeding fuel cells, which must have a precise hygrometric degree. However, in the state of the art, hydrogen and/or oxygen leaving an electrolyzer are saturated with water and carry with them droplets of water in suspension. The adjustment of the hygrometric degree of hydrogen and/or oxygen

30   leaving an electrolyzer requires one or more drying steps, typically a filtering step which eliminates the droplets and then a condensation step by cooling at low temperature thanks to a refrigerating system, which is generally energy consuming. It is also possible to proceed by producing dry gases and then controlling their hydration, for example by splashing or circulation in exchangers with a controlled water vapour

35   content. These techniques have a significantly high cost, both in terms of investment

4

and in terms of energy consumption.

Summary of the invention

It is an object of the present invention to solve the aforementioned problems of the prior

5   art, allowing to produce gaseous hydrogen or oxygen at controlled humidity levels.

This and other objects are fully achieved, according to a first aspect of the present invention, by virtue of a water electrolysis device having the features set forth in independent claim 1 and, according to another aspect of the present invention, by virtue of a water electrolysis method comprising the steps set forth in independent

10   claim 9.

Further advantageous features of the water electrolysis device according to the present invention are defined in the dependent claims.

In short, the invention is based on the idea of providing a PEM-type or AEM-type water electrolysis device wherein the current density and the water flow pumped into the

15   water supply compartment of the device are suitably controlled in such a manner as to adjust the humidity level in the gaseous hydrogen or oxygen at the outlet of the membrane water electrolysis cell to any desired value comprised between 0% and 100%. in other words, according to the present invention by suitably controlling the current density and the water flow pumped into the water supply compartment the

20   humidity level in the gaseous hydrogen or oxygen at the outlet of the membrane water electrolysis cell is adjusted to be equal to a desired value comprised between 0% and 100%.

The characteristics and the advantages of the present invention will be evident to those skilled in the art from the following detailed description, given purely by way of non-

25   limiting example.

Brief description of the drawings

In the following detailed description reference will be made to the appended drawings, wherein:

30   - Figure 1 is a cross-section view of a water electrolysis cell with polymer electrolyte membrane;

- Figure 2 is a schematic representation of a PEM water electrolysis cell with wet anode and cathode;

- Figure 3 is a schematic representation of a AEM water electrolysis cell with wet anode and cathode;

- Figure 4 is a schematic representation of a PEM water electrolysis cell with dry anode and wet cathode;

5   - Figure 5 is a schematic representation of an AEM water electrolysis cell with wet anode and dry cathode;

- Figure 6 is a graph showing the relationship between cell voltage and current density in a PEM water electrolysis cell for various operating temperatures, both in case of water circulation on both sides of the cell and in case of water circulation in the
10   hydrogen side only (a similar behaviour is observed experimentally with an AEM water electrolysis cell in case of water circulation in the oxygen side only);

- Figure 7 is a graph showing the typical impedance diagrams measured on a PEM water electrolysis cell when water is circulated in the hydrogen compartment only, at increasing cell voltages (the high frequency impedance related to electrochemical
15   reactions decreases but the low frequency part of the graphs shows mass transport-limitations);

- Figure 8 shows the current-voltage characteristic of an AEM water electrolysis cell;

- Figure 9 shows concentration overvoltage as a function of current density in an AEM water electrolysis cell; and

20   - Figure 10 is a schematic representation of two water electrolysis cells (one PEM and one AEM) connected in series to form a bi-cell to simultaneously produce hydrogen and oxygen at controlled humidity levels.

Detailed description

25   The innovative approach on which the present invention is based is to use a PEM water electrolysis cell (hereinafter also referred to simply as PEM cell) with dry anode for the production of oxygen at a controlled humidity level. Symmetrically, the same approach is to use an AEM water electrolysis cell (hereinafter also referred to simply as AEM cell) with dry cathode for the production of hydrogen at a controlled humidity
30   level.

Experience shows that for PEM or AEM cells fed by water circulation in both compartments, the current density does not show any saturation effect (i.e. no

tendency for the current density to approach a limit value). On the other hand, when these cells are supplied with water in only one compartment according to Figures 4 and 5, a phenomenon of current saturation appears (as shown in Figure 6) whose value depends on the type of polymer, the types of catalyst (anode and cathode), the operating temperature and the operating pressure. In the area of current density where the limitation of water transport appears, the impedance of the cell increases significantly (as shown in Figure 7), indicating a loss of efficiency.

The results in Figure 6 show that the diffusion rate of water through the membrane becomes kinetically limiting. The value of the saturating current density (maximum value of the current density that can be obtained) depends on several parameters including temperature, but also water pressure in the water supply compartment. When current density approaches the saturation value, all the water that flows through the membrane is electrolyzed on the opposite electrode, hence the idea of using these experimental results to produce more or less dry gases depending on the value of the current density.

To control the current density, and thus the hygrometric degree of the produced gases, it is necessary to determine the role of the main experimental parameters. For this purpose, it is necessary to build a physical-chemical model to account for the phenomenon of saturation in current density.

The innovative idea results from the analysis of flows of chemical species in membrane water electrolysis cells and the understanding of the equilibrium conditions between the water-saturated polymer membrane and the gas compartment in which the water content has to be controlled. From a microstructural point of view, polymer membranes (ionomers or polymers impregnated with an electrolyte) are biphasic materials comprising two nanostructured and interpenetrated phases (separate percolation of each of the two phases). The first hydrophobic phase consists in the carbon (or fluoro-carbon) skeleton of the polymer material. Water cannot dissolve in it. The second hydrophilic phase is constituted by the percolation of agglomerated ionic domains called "clusters" or "ionic clusters" which result from the organization in the form of inverted micelles of the ionized pendant chains. When this type of membrane is used in a polymer electrolyte water electrolysis cell (PEM or AEM), water is transported through the membrane into the hydrophilic phase.

The mechanisms of water transport through a polymer membrane are mainly of two types: (i) a purely diffusive transport whose driving force is a chemical potential gradient (resulting for example from a pressure gradient) which can be either local or

imposed on either side of the membrane; (ii) an electro-osmotic transport whose driving force is the electric current density resulting from the polarization (electric field) applied on either side of the membrane. The term "electro-osmotic flow" refers to the flow of water through the membrane during electrolysis due to the circulation of hydrated ions (charge carriers). The solvation water molecules of the ionic charge carriers circulating through the membrane during electrolysis are released into the compartment where the ionic species is consumed. The electro-osmotic flux can be measured in litres per hour or expressed by the number of solvation molecules (usually water) per each mobile ion (the proton H+ in a PEM membrane and the hydroxyl ion OH- in an AEM membrane).

The transport of water by diffusion and electro-osmosis through the membrane is governed by physical-chemical processes such as the Fourier's law of diffusion, the Darcy's law of flow in porous media, and the Faraday's law of conservation of electrical charges. When the water required for the operation of a water electrolysis electrode (oxygen anode, Figure 4, in the case of a PEM cell, and hydrogen cathode, Figure 5, in the case of an AEM cell) arrives at the catalytic layer through the membrane, there is a quantitative relationship between the water flow rate in the water supply compartment, the associated pressure drop, the membrane properties (thickness, equivalent weight, load carrier concentration, operating temperature T and pressure p) and the operating current density (often denoted as j and measured in A/cm^2). This proportionality relationship is determined in the following way using a mass balance.

i) Mass balance in water at the AEMWE cathode through a membrane

The amount of water that comes out of the membrane and flows into the cathodic compartment is equal to the amount of water that reaches through diffusion minus the amount of water that is consumed by the reaction and the amount of water that leaves by electro-osmosis.

ii) Fick's equation of order 1 (stationary state)

$$(a) \quad J_i = -D_i \nabla C_i \, ,$$

where J_i is the molar flux density of species i (in mole/(cm$^2 \cdot$s)), D_i is the diffusion coefficient of species i (in cm^2/s), and C_i is the molar concentration of species i.

The driving force of diffusion is the molar concentration gradient in species i.

iii) Definition of the coefficient of permeability P_i

Polymer membranes can be assimilated to a porous medium. The transport relationship is then expressed as a function of the coefficient of permeability P_m by the

8

following equation:

$$(b) \quad P_m = D \cdot S,$$

where D is the diffusion coefficient (in cm^2/s) and S is the solubility (in $mol/(cm^3 \cdot Pa)$).

The flow of water by diffusion is thus expressed by the following equation:

$$(c) \quad \frac{J_{H_2O}\left(\frac{mol}{s}\right)}{A(cm^2)} = Pm \frac{\Delta p}{L} = D_{H_2O} S_{H_2O} \frac{\Delta p}{L},$$

where L is the thickness of the membrane (in cm) and Δp is the pressure difference between the two compartments of the water electrolysis cell.

iv) Mass balance

The mass balance of water is therefore written as follows:

$$(d) \quad J_{H_2O}^{out} = +P_m \frac{\Delta p}{L} - \frac{j}{2F} - \frac{nj}{2F} = P_m \frac{\Delta p}{L} - \frac{j}{2F}(1+n),$$

where $J_{H_2O}^{out}$ is the water flow out of the membrane (in $mole(cm^2 \cdot s)$), n is the number of water molecules per molecule of charge-carrying ion, j is the current density (in A/cm^2), and F is the Faraday constant = 96485,33 (in $s \cdot A/mol$).

v) Condition that cancels the flow of water out of the membrane

In order to obtain a dry gas in the compartment where the water arrives by diffusion, it is necessary to find the conditions that cancel out the flow of water coming out of the membrane being, i.e. the conditions that ensure the following result:

$$(e) \quad J_{H_2O}^{out} = 0.$$

In this case, the current density j takes a particular value called limit current density and indicated j_L:

$$(f) \quad \frac{j_L}{2F}(1+n) = \frac{D_{H_2O}}{RT} \frac{\Delta p}{L},$$

where:

$$(g) \quad j_L = P_m \frac{\Delta p}{L} \frac{2F}{(1+n)} = P_m \frac{(p^{up} - p^{down})}{L} \frac{2F}{(1+n)}.$$

Assuming that one is looking for a dry gas in the cathodic compartment, the pressure p^{down} in this cathodic compartment must be equal to zero. By expressing p^{up} in relation to vacuum (dry gas), one obtains:

9

$$\text{(h)} \quad j_L = P_m \frac{p^{up}}{L} \frac{2F}{(1+n)} \ .$$

vi) Expression of the water pressure in the cell as a function of the flow rate of the
5   pumped water

The above equation (h) shows that the pressure p^{up} plays a key role in the process of
diffusional transport of water through the membrane, since it determines the amplitude
of the water transfer (driving force of the transfer). It is therefore necessary to know the
value of the pressure in the compartment where the water circulates. In practice, the
10   compartment in question contains a certain number of elements (PTL, grids) that
increase the pressure drop (D. Bessarabov, P. Millet, PEM Water Electrolysis,
Hydrogen and Fuel Cells Primers", B.G. Pollet Editor, 1st Edition, Elsevier (2018)).
There is a relationship of second order between the flow rate of the circulating water
and the pressure difference Δp across the cell. The quantitative relationship depends
15   on the internal hydraulic resistance of the cell. If this resistance is known, the flow
measurement gives access to the pressure difference Δp and thus to the average
pressure p^{up} in the cell. On the other hand, the compartment where oxygen is
produced may itself be under pressure. Depending on the technology used, the
pressure on the oxygen side may be close to or lower than that in the hydrogen
20   compartment. Pressure p^{up} is therefore equal to the pressure in the anode
compartment, due to the oxygen pressure and the hydraulic pressure drop.

vii) Mass transfer overvoltage during water electrolysis

From these considerations, it appears that when water is brought to the electrode
where it is consumed (the cathode in the case of an AEM cell) by transport through the
25   membrane rather than directly by pumping into the cathode compartment, there is a
critical current density, i.e. the above-mentioned limit current density j_L. The existence
of a limit current density j_L induces an electrical mass transport overvoltage. There are
analytical expressions of this overvoltage in the literature (and in particular in that
relating to fuel cells, a fuel cell being a type of cell whose electrochemical reaction is
30   powered by gas transport to the electrodes), for example (F. Barbir, PEM Fuel Cells,
Elsevier, 2005, p. 45-47):

$$\text{(i)} \quad \Delta U_{conc} = \frac{RT}{nF} ln \left(\frac{j_L}{j_L - j} \right) \ .$$

There are also empirical expressions such as:

$$\text{(j)} \quad \Delta U_{conc} = C\, exp\left(\frac{j}{D}\right),$$

5   where C and D are adjustable empirical coefficients.

viii) Mass transfer overvoltage during electrolysis of water

Taking p^{up} = 20 bar, it is possible to calculate, using equation (h), the value of the limit current density j_L that allows to obtain a dry gas in the cathodic compartment. Assuming P_m = 9,1 x 10^{-14} mol/(s·cm·Pa), L = 0,02 cm and n = 4, it follows that j_L =

10   0,35 A/cm². This is the current density which corresponds to the inflexion point in the graph of Figure 8. It should be noted here that for a given cell, when the water flow is changed, the position of the inflexion point and the two limits of the central region are shifted along the current density scale.

The following procedure can therefore be carried out to reach a target humidity level.

15   a) The cell/stack is placed on a typical test bench used for operation of water electrolyzers (D. Bessarabov, P. Millet, PEM Water Electrolysis, "*Hydrogen and Fuel Cells Primers*", B.G. Pollet Editor, 1st Edition, Elsevier (2018)).

b) The water flowing across the water supply compartment is set to the nominal value which is usually determined by the maximum acceptable temperature difference

20   between cell inlet and outlet (A. Villagra, P. Millet, "*An analysis of PEM water electrolysis cells operating at elevated current densities*", Int. J. Hydrogen Energy, 44(20) (2019) 9708-9717).

c) The cell voltage to be applied is determined from the cell voltage/current density characteristic curve of the cell/stack (a typical example of which is shown in Figure 8).

25   There are two characteristic points: the first one at 0,25 A/cm² and 1,6 Volt and the second one at 0,45 A/cm² and 1,9 Volt. These two points delimit the current density range in which it is possible to adjust the humidity level. The Y-axis of the graph of Figure 8 expressed in Volt can be replaced by a scale in water %.

d) Then the desired cell voltage is applied to the cell. In this example, when the cell

30   voltage is higher than 1,6 Volt, 100% hydrated gas is produced; when the cell voltage is higher than 1,9 Volt, dry gas is produced; and when the cell voltage is comprised between 1,6 and 1,9 Volt, the humidity level of the gas is between 0 and 100% and proportional to the cell voltage. This is a not linear proportionality as shown in Figure 8.

11

The water content in the gas comes from the membrane, which is saturated with water. The production of a dry gas on one side of the membrane is therefore difficult to achieve because the water present on the surface of the membrane in contact with the dry gas tends to evaporate (in this case the gas produced contains a water vapour pressure) or even (when the water flow is too high) to pass directly as liquid water into the compartment where the gas is produced, the hygrometric degree of which we are trying to control. It is therefore necessary to find a way to allow the liquid water that comes through the membrane to reach the catalytic layer but to prevent the too rapid evaporation of water from the catalytic layer. For this purpose, according to an aspect of the present invention a water retainer can be introduced into the catalytic layer of the PEM or AEM cell where the water molecule is dissociated. The water retainer is a chemical compound, preferably solid, hydrophilic, with a high storage capacity of liquid water (therefore present in the form of small particles, for example nanoparticles, with high porosity). This material must have a water sorption isotherm at the operating temperature and pressure of the cell with a low water vapour pressure.

Examples of water retaining materials are metal oxides (such as silica SiO_2, titanium oxide TiO_2), superabsorbent polymeric materials (e.g. polyelectrolytes such as sodium polyacrylates), cellulose ethers, methyl cellulose, hydoxyethyl methyl cellulose, hypromellose or hydroxypropyl methyl cellulose (HPMC), certain clays (natural silicate or alumino-silicate based minerals), or any other material with marked hydrophilic properties. The content of water retaining materials in the catalytic layer must be optimized according to the intended application and the desired moisture content.

The present invention describes a process allowing the production of hydrogen or oxygen with a controlled humidity level between 0% (dry gas) and 100% (wet gas saturated with water). The process is carried out by means of a membrane-type water electrolysis device containing any number of elementary cells, which may be of any nature, constituent materials, size and shape (for example planar, cylindrical or even spherical). The mass balances carried out on the electrodes in contact with the gases whose humidity level must be controlled show that it is necessary to control the water electrolysis cell by controlling two key parameters: (i) the water pressure in the opposite compartment so as to control the diffused water transport (water flow rate through the membrane), and (ii) the current density that sets the electro-osmotic flow of water.

A first aspect of the present invention is based on the analysis and understanding of the mechanisms of water transport through a polymer membrane, which are of two

12

types: (i) a diffusive transport whose driving force is a pressure gradient; and (ii) an electro-osmotic transport whose driving force is the electric current density. According to the technical characteristics indicated above, the current-voltage curve has a characteristic limit current density. By operating the cell at a current density higher than the limit current density, it is possible to produce a dry gas. By operating the cell at a current density close to the limit current density, a gas with controlled humidity can be produced. By operating the cell at a current density below the limit current density, it is possible to produce a gas saturated with water vapour or even a two-phase water-gas mixture. The control of the current density with which the cell is operated therefore allows to adjust the humidity level (hygrometric degree) of the produced gases according to the needs.

Another aspect of the present invention is based on the introduction into the catalytic layer where the water is consumed of a water-retaining hydrophilic additive that will prevent the evaporation of water from the membrane into the dry gas and will make it possible to control the humidity level (hygrometric degree) of the gas produced.

A further aspect of the present invention is based on the provision of a stack of cells alternating proton and anion conduction membranes. Thus, the same reactor allows the simultaneous production of hydrogen and oxygen at a controlled hygrometric degree.

The results obtained with membrane water electrolysis cells controlled according to the invention are provided below by way of examples.

Example 1

In a first example, the current-voltage characteristic of an AEM water electrolysis cell powered by water transport through the membrane was measured (Figure 7) and modelled using the mass balance equation (h) presented earlier.

Example 2

In a second example, two water electrolysis cells (one PEM and one AEM) were connected in series to form a bi-cell to simultaneously produce hydrogen and oxygen at controlled humidity levels (Figure 10). Several such bi-cells can be stacked in any number to adjust the capacity to produce moisture-controlled gases as required.

The present invention has been disclosed herein with reference to some preferred embodiments thereof, It is however clear that other embodiments may be provided for, which share with the ones herein disclosed the same inventive idea, as defined by the appended claims.

13

CLAIMS

1. Electrolysis device for the production of gaseous hydrogen or oxygen at a controlled humidity level, the device comprising

- at least one water electrolysis cell (10) having a ion-conducting membrane, said at least one water electrolysis cell (10) being actuated by diffusional transport of water through said membrane,

- liquid water supply means for supplying liquid water in a water supply compartment of said at least one water electrolysis cell (10) opposite to the electrode where electrolytic decomposition of the water takes place, and

- control means configured to control the current density and the water flow pumped by said water supply means into said water supply compartment to adjust the humidity level in the gaseous hydrogen or oxygen at the outlet of said at least one water electrolysis cell (10) to a desired value comprised between 0% and 100%.

2. Device according to claim 1, wherein said at least one water electrolysis cell (10) includes, in addition to said membrane:

- a frame made of non-conductive engineering polymer material having fluid distribution and collection channels and seals,

- a cathodic catalytic layer and an anodic catalytic layer,

- a cathodic porous layer and an anodic porous layer,

- a cathodic porous spacer and an anodic porous spacer, and

- two metallic bipolar end plates.

3. Device according to claim 2, wherein said cathodic catalytic layer and anodic catalytic layer include a water-retaining hydrophilic additive.

4. Device according to claim 2 or claim 3, wherein the membrane is made of a polymeric or inorganic proton-conducting material, wherein the cathodic catalytic layer comprises a platinum-based catalyst and a polymeric binder of the same chemical nature as said membrane, and wherein the anodic catalytic layer comprises an iridium oxide-based catalyst and a polymeric binder of the same chemical nature as said membrane.

5. Device according to claim 2 or claim 3, wherein the membrane is made of a polymeric or inorganic material anionically conductive by hydroxyl ions, wherein the cathodic catalytic layer comprises a catalyst based on oxides of Ni, Co, Fe or their

14

mixtures, and a polymer binder of the same nature as said membrane, and wherein the anodic catalytic layer comprises a catalyst based on oxides of Cu, Co, Ni, Mn or their mixtures, and a polymeric binder of the same nature as said membrane.

6. Device according to any one of claims 2 to 5, wherein either or both of the catalytic layers are deposited directly on the membrane or on the surface of the porous layers on either side of said membrane.

7. Device according to any one of claims 2 to 6, wherein either or both of the catalyst layers contain a water-retaining hydrophilic additive, such as silica (SiO_2), or titanium oxide (TiO_2), or polyelectrolytes such as sodium polyacrylates, or cellulose ethers, or methyl cellulose, or hydoxyethyl methyl cellulose, or hypromellose or hydroxypropyl methyl cellulose (HPMC), or certain silicate or alumino-silicate based clays, or combinations thereof.

8. Device according to any one of the preceding claims, containing one or more PEM water electrolysis cells and/or one or more AEM water electrolysis cells.

9. Device according to any one of the preceding claims, wherein said control means are configured to apply between the two electrodes of said at least one water electrolysis cell (10) an electric potential difference in the range of 1,5 to 3,0 V, corresponding to a current density between 0 and 10 A/cm^2.

10. Method for producing gaseous hydrogen or oxygen at a controlled humidity level by means of at least one water electrolysis cell (10) which has a ion-conducting membrane and is actuated by diffusional transport of water through said membrane, the method comprising the steps of:

a) supplying liquid water in a water supply compartment of said at least one water electrolysis cell (10) opposite to the electrode where electrolytic decomposition of the water takes place, and

b) controlling the current density and the water flow pumped into said water supply compartment to adjust the humidity level in the gaseous hydrogen or oxygen at the outlet of said at least one water electrolysis cell (10) to a desired value comprised between 0% and 100%.
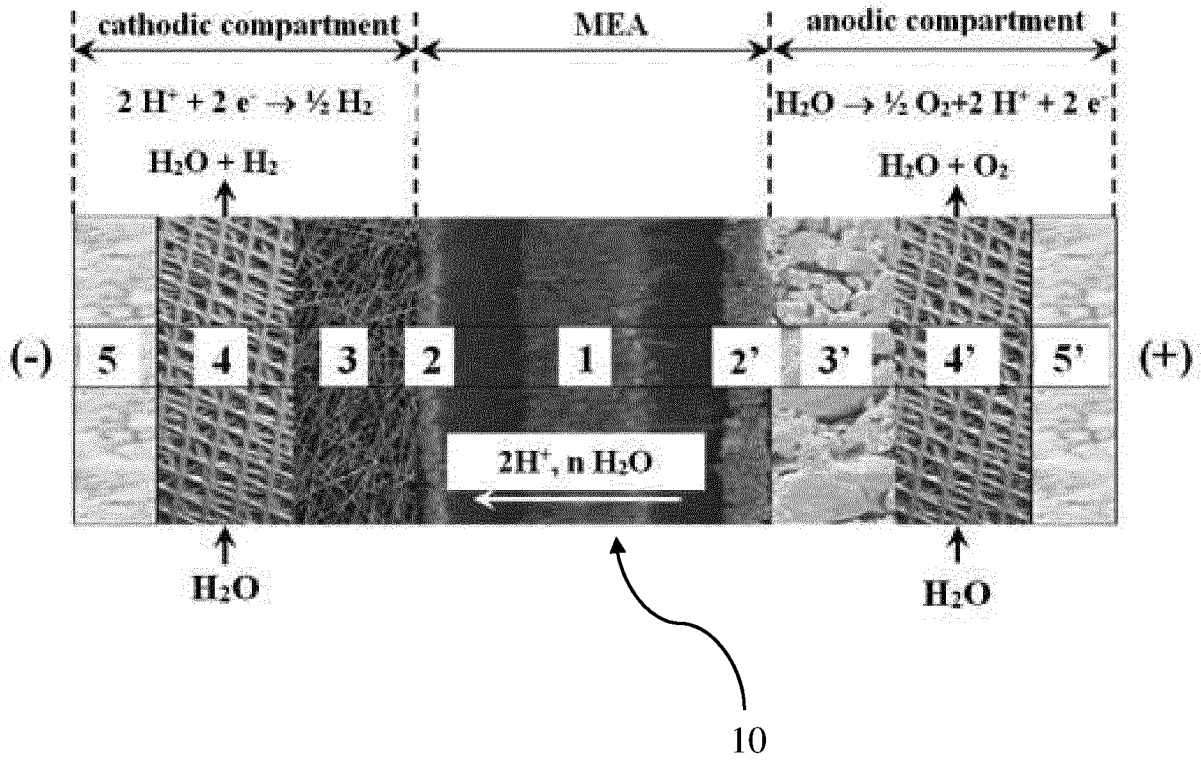
FIG. 1

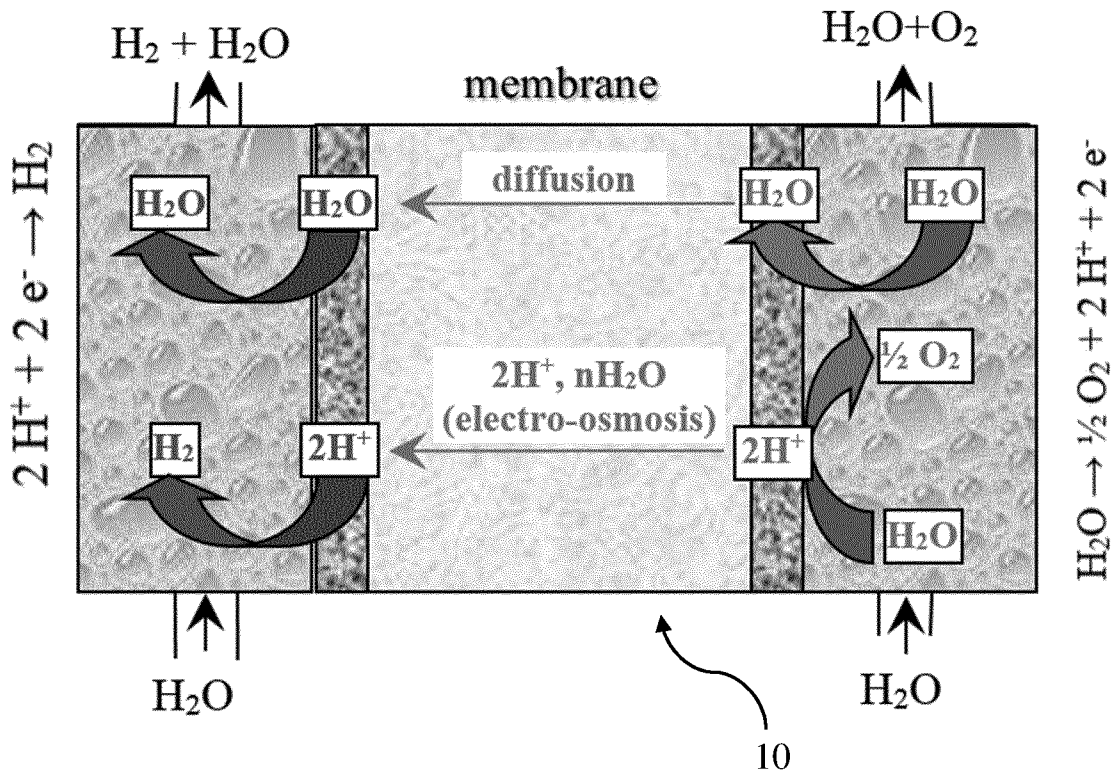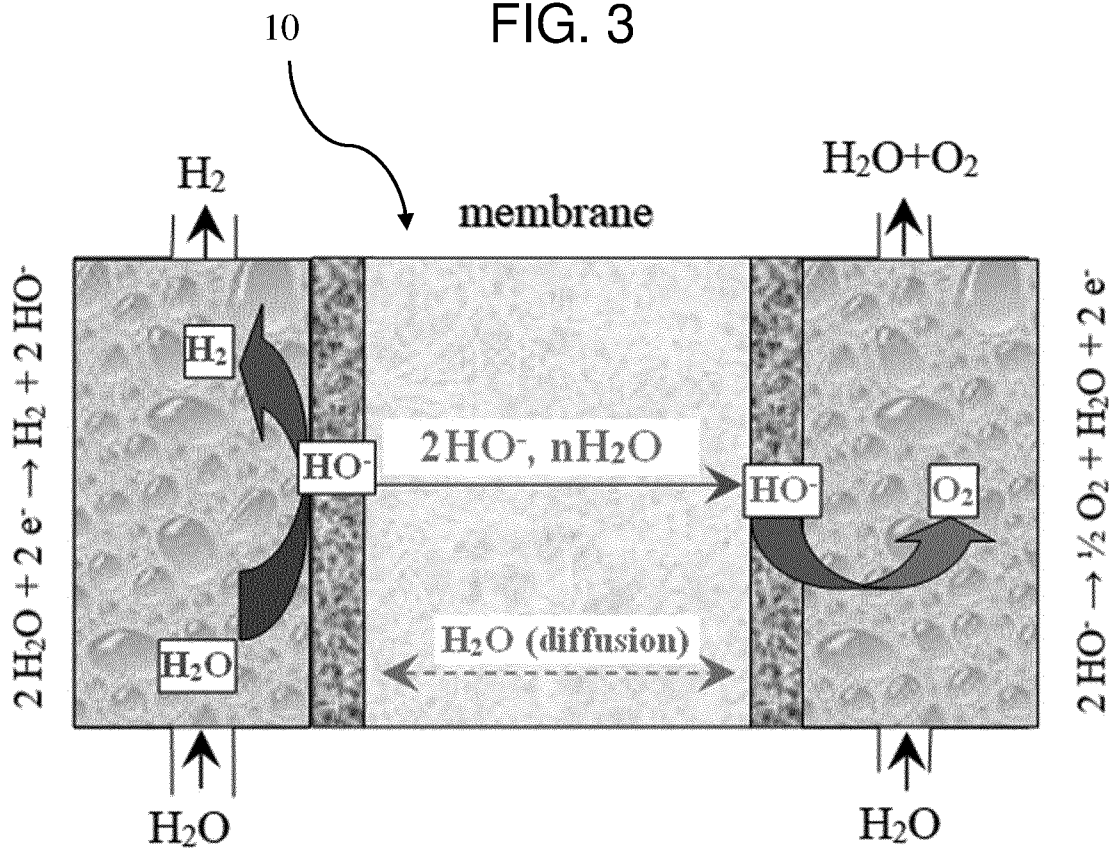cathodic compartment · MEA · anodic compartment

$2\,H^+ + 2\,e^- \rightarrow \frac{1}{2}\,H_2$

$H_2O \rightarrow \frac{1}{2}\,O_2 + 2\,H^+ + 2\,e^-$

$H_2O + H_2$

$H_2O + O_2$

(-) 5 4 3 2 1 2' 3' 4' 5' (+)

$2H^+, n\,H_2O$

H_2O

H_2O

10

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

water circulation in the H₂ compartment only
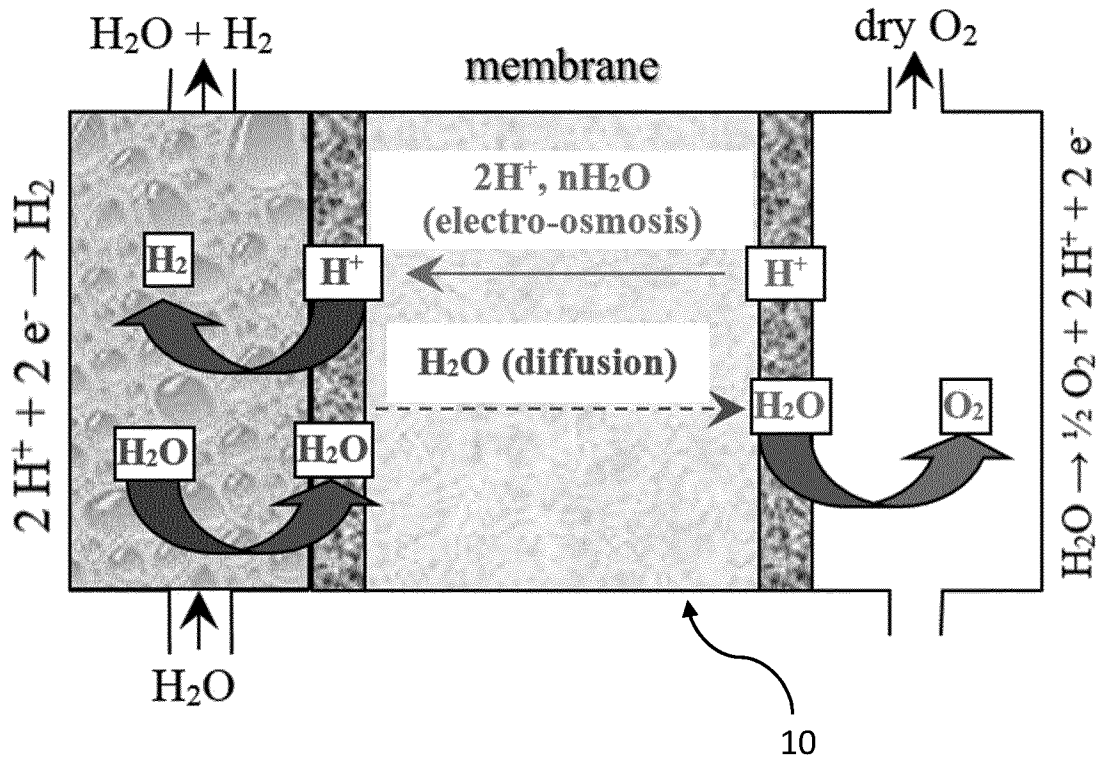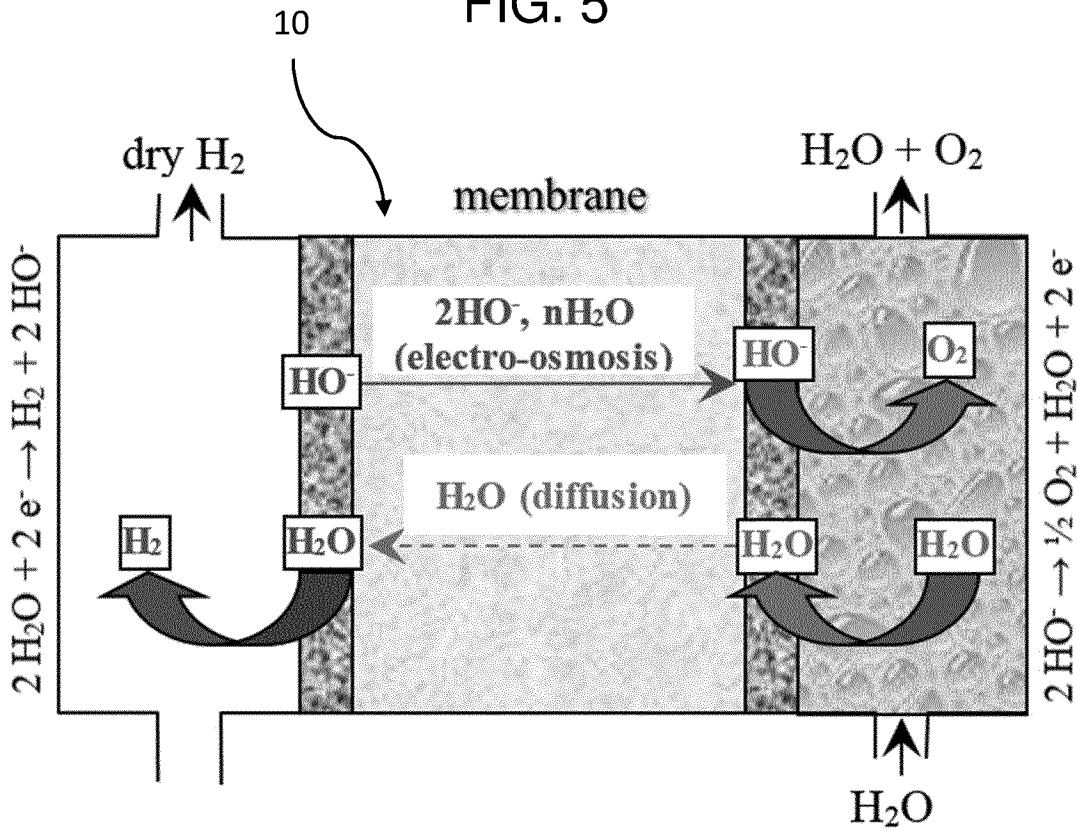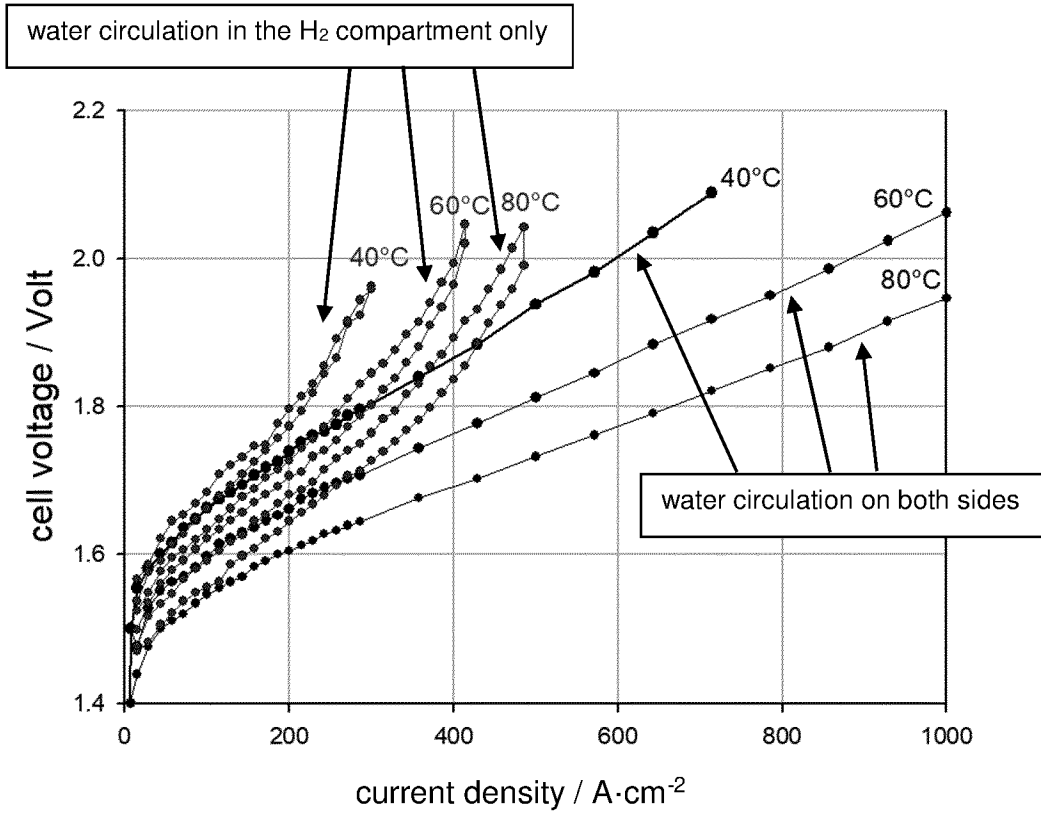
FIG. 7
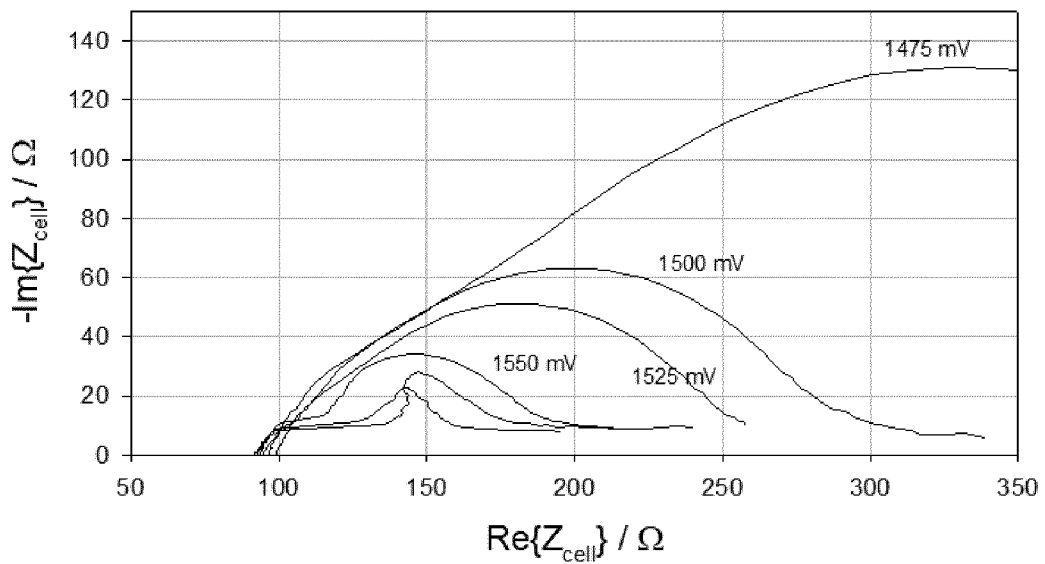
FIG. 8
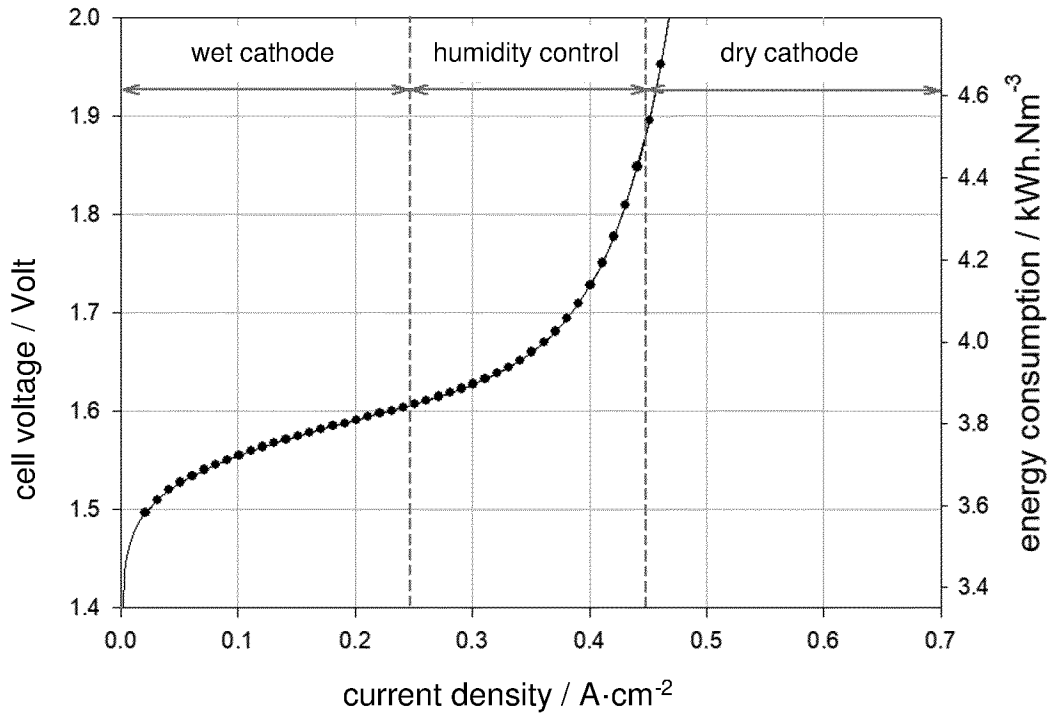
FIG. 9
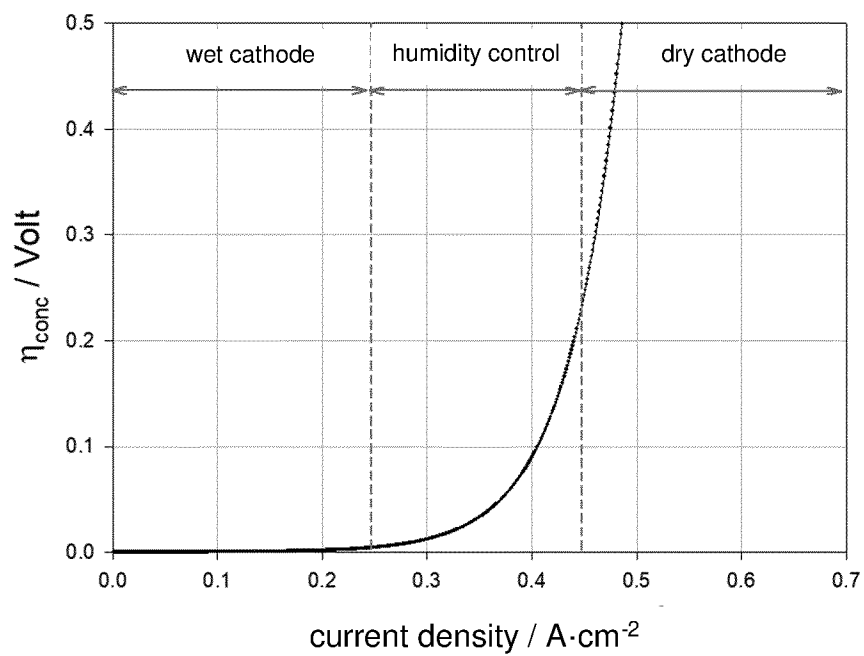
FIG. 10
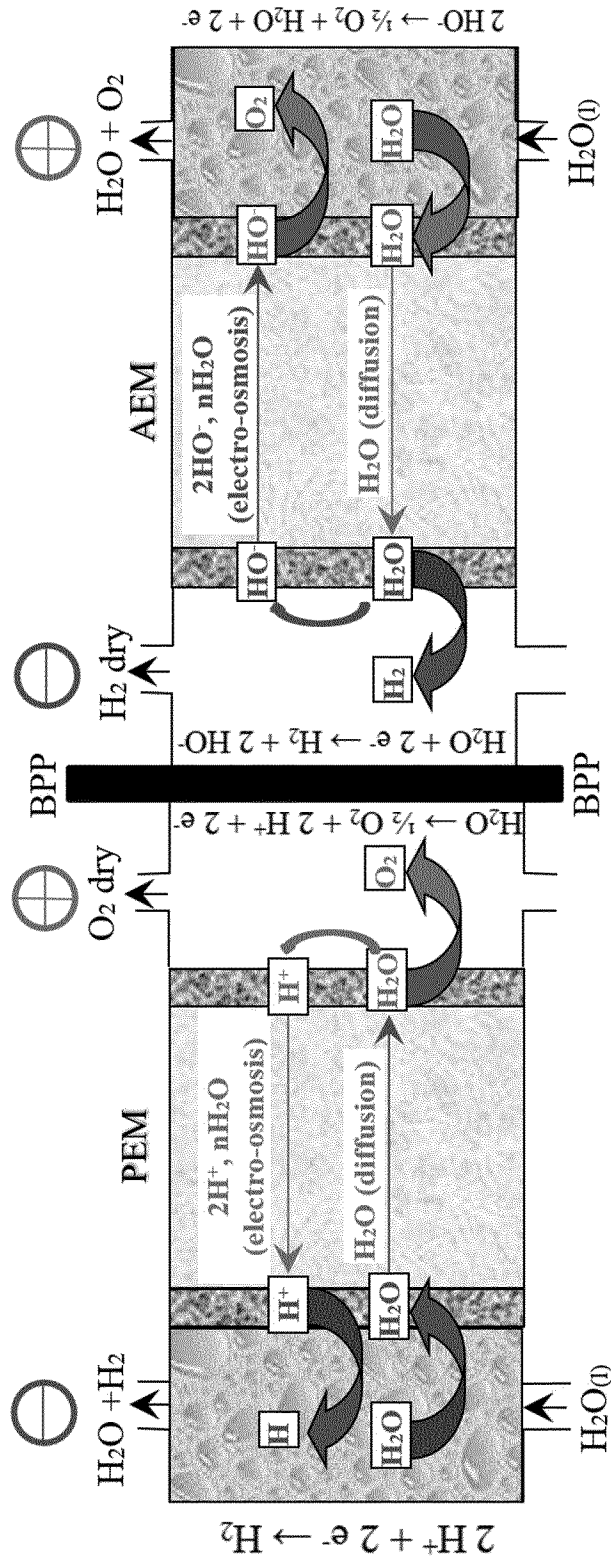
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C25B1/04   C25B9/19   C25B15/023   C25B15/025
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 1 312 321 C (XU WENXING [CN]) 25 April 2007 (2007-04-25)	1,2,4-6, 8-10
A	the whole document	3,7
X	EP 3 647 468 A1 (H2B2 ELECTROLYSIS TECH S L [ES]) 6 May 2020 (2020-05-06)	1,2,4-6, 8-10
A	the whole document	3,7
A	US 2012/241315 A1 (YOSHINAGA NORIHIRO [JP] ET AL) 27 September 2012 (2012-09-27) the whole document	1-10
A	US 6 685 821 B2 (GINER ELECTROCHEMICAL SYSTEMS [US]) 3 February 2004 (2004-02-03) the whole document	1-10
A	US 2019/192806 A1 (BAHAR BAMDAD [US] ET AL) 27 June 2019 (2019-06-27) the whole document	1-10

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 February 2022	23/02/2022

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Juhart, Matjaz

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT
Information on patent family members

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
CN 1312321	C	25-04-2007	NONE		
EP 3647468	A1	06-05-2020	EP	3647468 A1	06-05-2020
			WO	2018189409 A1	18-10-2018
US 2012241315	A1	27-09-2012	CN	102688664 A	26-09-2012
			JP	5638433 B2	10-12-2014
			JP	2012201911 A	22-10-2012
			KR	20120109299 A	08-10-2012
			KR	20140125330 A	28-10-2014
			US	2012241315 A1	27-09-2012
			US	2014339097 A1	20-11-2014
US 6685821	B2	03-02-2004	US	2003062268 A1	03-04-2003
			WO	03021006 A1	13-03-2003
US 2019192806	A1	27-06-2019	NONE		