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(54) Title **Polymer electrolyte membrane (PEM) water electrolyser cell, stack and system and a method for producing hydrogen in said PEM water electrolyser system**

(56) References Cited:

US 2011/198232 A1
WO 2009/072838 A2
WO 2008/138048 A1
US 2017/321329 A1
US 5622609 A
US 6562446 B1

(57) Abstract

The present invention relates to a polymer electrolyte membrane water electrolyser cell for hydrogen production. The cell comprises a polymer electrolyte membrane separating the electrolyser cell in an anode compartment and a cathode compartment, an anode catalyst layer and a cathode catalyst layer, deposited on either side of the membrane. The anode compartment is supplied with humidified air, and the cathode compartment is supplied with ion exchanged water, and a thin polymer electrolyte membrane having thickness of less than 120 μm is used. The invention also relates to a polymer electrolyte membrane water electrolyser stack and a polymer electrolyte membrane water electrolyser system. Further, the invention relates to a method for producing hydrogen in the polymer electrolyte membrane water electrolyser system.

Technical field

The invention relates to a polymer electrolyte membrane (PEM) water electrolyser system capable of producing hydrogen and a method for operating this PEM electrolyser system. More specifically, the invention relates to a PEM water electrolysis cell and stack of cells and the operation thereof.

Background/prior art

Water electrolysers today are operated with a stack efficiency around 65-70% (higher heating value HHV) which results in a demand of about 55 kWh of electricity for 1 kg H_2. Of the 55 kWh, about 50 kWh is used by the electrolysis process and 5 kWh by the balance of plant. In most water electrolyser systems, the cost of electricity can amount to up to 80% of the cost of the produced hydrogen and an increase in the efficiency of the water electrolyser stack will improve both the overall primary electrical energy consumption and the total cost of hydrogen.

Current PEM electrolysers are limited in efficiency by mainly two factors:

1. The overpotential on the anode
2. The ohmic resistance in the polymer membrane.

The last decade, there has been very little improvement in the overall efficiency of these types of water electrolysers and most of the research and development effort has been put into reducing the production costs by increasing size and improving manufacturability.

PEM water electrolysers generate hydrogen by electrolytically decomposing water and are currently operated by feeding water on the anode side, which by an electrochemical reaction is converted to oxygen, protons and electrons (see e.g. US patent application 2003/0230495 A1). The protons migrate through the membrane and are reduced through an electrochemical reaction with electrons to hydrogen on the cathode. Water is also transported through the membrane due to electroosmotic drag caused by the flux of protons. In addition to these main transport phenomena, hydrogen and oxygen are also diffusing through the membrane due to the difference in partial pressures of the gases on each side of the membrane.

In current commercial designs of PEM electrolysers, the proton conducting membrane must be relatively thick (usually no less than 150 microns) as the hydrogen diffusing through the membrane is mixed with the oxygen evolved on the anode and will form explosive mixtures if this hydrogen transport is too high compared to the volume of oxygen being produced. These thick membranes cause a significant ohmic resistance and reduce the efficiency of the process by about 15%.

US 2011/198232 A1 relates to a high-differential-pressure water electrolysis cell. This electrolysis cell comprises a bilayer membrane including a platinum impregnated ion-exchange membrane layer and an untreated ion-exchange layer. WO 2009/072838 A2 describes a hydrogen and oxygen generator for internal combustion engines. WO2008/138048 A1 describes a conventional PEM water electrolyser cell wherein the anode chamber is provided with water and the cathode chamber is provided with air. US 5622609 A describes an electrochemical cell having an oxide growth resistant current distributor. The current distributor is useful in a process for converting anhydrous hydrogen halide to a halogen gas or in an aqueous electrochemical process. US 6562446 B1 relates to a multi-layer proton-conductive polymer electrolyte membrane used in a polymer electrolyte fuel cell.

It is an object of the present invention to reduce the energy consumption and consequently reduce the cost of hydrogen produced.
Another object of the present invention is to avoid the formation of flammable or explosive mixtures of oxygen and hydrogen in the electrolyser.

Short summary of the invention

The present invention provides a polymer electrolyte membrane (PEM) water electrolyser cell for hydrogen production according to claim 1. The PEM water electrolyser cell comprises a polymer electrolyte membrane separating the electrolyser cell in an anode compartment and a cathode compartment. An anode catalyst layer and a cathode catalyst layer are applied and attached to opposite sides of the membrane. The anode catalyst layer and the cathode catalyst layer comprise catalysts in powder form.

The anode compartment has an inlet for supply of humidified air, and the cathode compartment has an inlet for supply of ion exchanged water. The thickness of the polymer electrolyte membrane is less than 120 µm, preferably in the range 5 to 75 µm, more preferred from 15 to 60 µm.

The humidified air may have a relative humidity (RH) above 75% RH. The humidified air may be saturated with water. Optionally, supersaturated air is used. The temperature of the supplied air and the relative humidity values are at nominal operating temperature of the electrolyser of 50 to 90 °C.

Further, the present invention provides a PEM water electrolyser stack according to claim 3. The stack comprises a plurality of polymer electrolyte membrane water electrolyser cells according to the invention, connected in series.

Further, the invention provides a PEM water electrolyser system according to claim 4. The system comprises the PEM electrolyser stack according to the invention and a water and oxygen management system, a hydrogen gas management system, a water input system, mounting and packaging cabinetry subsystem, a ventilation system, power electronics and power supply, system controls and instrumentation, and a humidified air supply and humidification system.

Further, the invention provides a method for producing hydrogen in the water electrolyser system according to claim 5.

The method comprises:

supplying ion exchanged water to the cathode compartment,

supplying humidified air to the anode compartment,

applying a direct electric current to the water electrolyser cell,

permitting water molecules from the cathode compartment to diffuse through the polymer electrolyte membrane into the anode compartment,

oxidizing water molecules at the anode catalyst layer into protons and oxygen, permitting the protons to migrate through the polymer electrolyte membrane into the cathode compartment,
reducing the protons at the cathode to produce hydrogen.

Figures

Figure 1 shows a membrane electrode assembly, MEA, according to the state of the art.
Figure 2 shows a membrane electrode assembly, MEA, according to the invention.
Figure 3 is a schematic diagram of a PEM water electrolyser system.
Figure 4 is a diagram showing cell voltage, current density and anode side gas composition during an electrolyser test.

Detailed description of the invention

The objects and features of the invention can be better understood with reference to the drawings described below.
Figure 1 shows a conventional membrane electrode assembly (MEA) of a PEM water electrolyser cell. The main components of the MEA are the proton exchange membrane and a cathode and an anode deposited on either side of the membrane. Ion exchanged water is fed to the anode compartment of the cell. A small fraction of the water is consumed in the electrochemical reaction on the anode and is converted to oxygen, protons and electrons:

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

The protons migrate through the polymer electrolyte membrane from the anode side to the cathode side and by a phenomenon known as electroosmotic drag, carries a significant portion of liquid water (H_2O(drag)) from the anode side to the cathode side of the membrane. The remaining water in the anode compartment exits the cell together with the produced oxygen gas and some hydrogen and water ((H_2O(diff)) diffused through the membrane from the cathode side.
The water is separated from the oxygen and hydrogen gas, cooled and led back to a storage from where it is again fed back to the cell.

The water (H_2O(drag)) transported with the protons from the anode to the cathode compartment exits the stack with the produced hydrogen gas, and is separated from the hydrogen and then injected back to the anode water circuit through a controllable valve (not shown).
Hydrogen gas is produced on the cathode side:

$2e^- + 2H^+ \rightarrow H_2$

In addition to the water transport, oxygen and hydrogen (O_2(diff) and H_2(diff)) are diffused/transported through the membrane due to the partial pressure gradient of the gases across the membrane and as dissolved gas in the transported water. This gas flux across the membrane and the consequent mixing of hydrogen and oxygen is in state of the art PEM water electrolysers one of the main design and operational constraints: As only a small amount of hydrogen in oxygen is needed to form flammable and/or explosive gas mixtures, the hydrogen transported through the membrane will exceed this level if the oxygen production on the anode is too low (low current densities) or the transport of hydrogen is too high (thin membrane and/or high permeability).

This hydrogen crossover problem is in state of the art PEM water electrolysers remedied by using a thick membrane (above 120 µm), preferably made of perfluorosulfonic acid (PSFA) polymers, such as Nafion 117, to effectively reduce the hydrogen diffusion through the membrane. Another solution is to introduce hydrogen/oxygen recombination catalysts such as platinum or palladium into the membrane, which act as reaction sites for local recombination of oxygen and hydrogen to water, preventing the diffusing gases to reach the other electrode compartment and entering the gas phase. However, in order to have the necessary amount of recombination catalyst and time for the recombination reaction to take place, it is probably still necessary to have a significant thickness of the membrane. Thus, state of the art water electrolysers use polymer electrolyte membranes with thicknesses of 125 microns (Nafion 115 equivalent) or higher.

The use of such thick membranes introduces a significant ohmic resistance and consequently a lower efficiency of the electrolyser, especially at current densities above 1 Acm^{-2}.

The present invention provides a system where the reactant water is supplied to the anode by a combination of water diffusion from the cathode compartment and saturated or supersaturated air at the anode instead of by liquid water supplied to the anode. Figure 2 shows a membrane electrode assembly (MEA) of the PEM water electrolyser cell according to the invention. Air with water vapour ($H_2O_{(g)}$) is supplied on the anode side. Water molecules react on the anode and are converted to oxygen, protons and electrons:

$$H_2O \text{ -> } 2e^- + 2H^+ + ½O_2$$

The remaining water in the anode compartment exits the cell together with air, the produced oxygen gas and some hydrogen and water vapour (($H_2O(g)$)).
Ion exchanged water ($H_2O(l)$) is supplied on the cathode side and a portion of this water diffuse through the membrane to the anode side. There is a net transport of water to the anode side. Hydrogen produced on the cathode side exits the cell together with the remaining water which is separated from the hydrogen, purified and recycled to the cathode compartment.

This seemingly small change in system operation have several potential benefits:

1. The supply of large amounts of air to the anode will effectively dilute the hydrogen diffusing through the membrane to levels far away from the explosion limit (LEL) of about 4 mol% opening up the possibility of reducing the membrane thickness significantly (to less than 25 microns). The increased gas volume on the anode will also increase the operating window of the electrolyser, allowing operation at much lower currents than current systems.
2. An air environment in the anode will reduce the partial pressure of oxygen, reducing the reversible potential of the electrolyser (increasing efficiency) and reducing the oxygen diffusion through the membrane.
3. The reduced oxygen partial pressure and the lower oxygen transport to the cathode will also potentially reduce the corrosive environment and reduce

formation of hydrogen peroxide on the cathode, which will be positive for the overall lifetime of the cell.

The difficulty with operating a PEM electrolyser with humidified air is to supply sufficient water to accommodate the electrochemical reaction and simultaneously keep the membrane fully humidified to keep the proton conductivity high. Using a sufficiently thin membrane will make this easier as back diffusion of water from the cathode to the anode increases significantly.

A successful implementation of these innovations may have the following main impact.

- A 15% reduction of the electricity consumption of the electrolyser from about 50 kWh/kg H_2 to 42.5 kWh/kg H_2.
- The reduction of electricity usage will lead to a reduction of the cost of hydrogen with about 10-15 %, depending on the cost of electricity and annual operating hours, or about 4 NOK/kg H_2.

Secondary impacts

- Reduced energy consumption will lead to less heat production and consequently less need for cooling systems.
- Reduced use of expensive perfluorinated ionomer will reduce the cost of the MEAs used in PEM water electrolysers.

Figure 3 shows a PEM water electrolyser system according to the present invention. In this system, air is supplied via a blower or compressor (10) to an air humidifier (11) configured to direct humidified air to the PEM electrolyser stack (12) on the anode side so that the humidified air is distributed evenly over the surface of the anode electrode so as to dilute hydrogen gas permeating from the cathode to a level below 1 volume %. In addition, liquid water is supplied to the cathode compartment of the PEM water electrolyser stack (12). This combination is vital to secure the necessary water needed for the oxygen evolution reaction on the anode and to ensure a high water content in the membrane to retain a high proton conductivity. Ion exchanged water is supplied from a water purification device (17). Hydrogen produced exits the PEM water electrolyser stack (12) together with water. Hydrogen and water is separated in a hydrogen/water separator (13). The hydrogen flows through a deoxidizer/dryer (14). The separated water is recycled to the water purification unit (17) and into the PEM water electrolyser stack (12). A circulation pump (15) and a heat exchanger (16) may be included in the circulation line.

The use of humidified air on the anode enables use of thinner polymer electrolyte membrane. Ideal PEM membranes should have low ionic resistance, high mechanical integrity for differential pressure operation, low hydrogen permeation, no chemical or mechanical degradation with time, high temperature stability and low cost.
Perfluorosulfonic acid (PSFA) polymers, such as Nafion®, are preferred materials for PEM membranes. In the present invention, the thickness of such membranes should be less than 120 microns, preferably from 5 to 75 microns, even more preferred in the range 15 to 60 microns.
The preferred thickness is depending on the quality of the membrane material and operating pressures, and thus, the thickness should be optimized in each case.

Traditionally, metallic platinum is used for the hydrogen evolution reaction at the cathode and metallic iridium or iridium oxide is use for the oxygen evolution reaction at the anode.
Preferably, the membrane is also functionalized with a recombination catalyst to reduce the oxygen crossover to the cathode compartment and to contribute to an additional humidification of the membrane by forming water inside the membrane. Examples of such recombination catalysts are palladium or platinum nanoparticles.

Preferably, the membrane includes reinforcing materials.
Preferably, ion exchanged water of type 1 ASTM D1193-6 is used in water electrolysers.

Experiment

An experiment, see figure 4, was performed using a MEA based on a Nafion 212 membrane (50 micron thickness) and mounted in a 25 cm^2 electrolyser test cell. The test cell was connected to a PEM electrolyser test station from Greenlight Technologies.

During the first two hours of the experiment, the cell was operated at 60 °C in conventional mode at $1 Acm^{-2}$ with water circulation on the anode and cathode. The concentration of hydrogen in oxygen was continuously monitored and showed a steady state value of about 2 vol % at the anode side. After two hours, the operation was changed and $9 \, l \, min^{-1}$ of humidified air (100%RH) was supplied to the anode while liquid water was supplied to the cathode. The hydrogen concentration in the outgoing gas from the anode immediately drops to undetectable (below 0.1 %) levels while the cell voltage and current of the electrolyser is constant.

After 5 hours, the effect of current density was investigated. The current density was varied from 0.01 to $2 Acm^{-2}$ and no detectable amounts of hydrogen in the outgoing anode gas was detected. As a comparison, the cell was turned back to conventional operation with water on both anode and cathode and the hydrogen concentration quickly increased to about 2 vol% or higher (at low current density). After eight hours of operation, the cell was shut down and the experiment ended.

This experiment clearly demonstrates that a PEM electrolyser with a thin membrane can operate with only humidified air supplied to the anode inlet with the same performance as a cell supplied with liquid water on the anode, but with significantly lower hydrogen concentrations in the produced gas on the anode.

Claims

1. A polymer electrolyte membrane water electrolyser cell for hydrogen production, comprising

   a polymer electrolyte membrane separating the electrolyser cell in an anode compartment and a cathode compartment,

   an anode catalyst layer and a cathode catalyst layer, deposited on either side of the membrane,

   wherein the anode compartment is configured to be supplied with humidified air, and the

   cathode compartment is configured to be supplied with ion exchanged water, and

   the polymer electrolyte membrane has a thickness in the range from 5 to 75 µm.

2. The electrolyser cell of claim 1, wherein the thickness of polymer electrolyte membrane is in the range from 15 to 60 µm.

3. A polymer electrolyte membrane water electrolyser stack, comprising a plurality of polymer electrolyte membrane water electrolyser cells according to claim 1 or 2, connected in series.

4. A polymer electrolyte membrane water electrolyser system, comprising

   a water and oxygen management system,

   a hydrogen gas management system,

   a water input system,

   mounting and packaging cabinetry subsystem,

   a ventilation system,

   power electronics and power supply,

   system controls and instrumentation,

   the system further comprising:

   the polymer electrolyte membrane water electrolyser stack of claim 3, and a humidified air supply and humidification system.

5. A method for producing hydrogen in a polymer electrolyte membrane (PEM) water electrolyser system according to claim 4,
the method comprising:
applying a direct electric current to the water electrolyser cell,
permitting water molecules from the cathode compartment to diffuse through the polymer electrolyte membrane into the anode compartment,
oxidizing water molecules at the anode catalyst layer into protons, oxygen and electrons,
permitting the protons to migrate through the polymer electrolyte membrane into the cathode compartment,
reducing the protons at the cathode catalyst layer to produce hydrogen,
supplying ion exchanged water to the cathode compartment, and
supplying humidified air to the anode compartment.

6. The method of claim 5, wherein the humidified air has a relative humidity (RH) above 75% RH at a nominal operating temperature of the electrolyser.

7. The method of claim 5 or 6, wherein the humidified air is supersaturated air.

8. The method of any of claims 5 to 7, wherein the thickness of the polymer electrolyte membrane is the range from 15 to 60 μm.

Patentkrav

1. Polymerelektrolyttmembran-vannelektrolysørcelle for hydrogenproduksjon, omfattende

en polymerelektrolyttmembran som separerer elektrolysecellen i et anodekammer og et katodekammer,

et anodekatalysatorlag og et katodekatalysatorlag, anbragt på hver sin side av membranen,

hvor anodekammeret er konfigurert til å bli tilført fuktet luft, og

katodekammeret er konfigurert til å bli tilført ionebyttet vann, og

polymerelektrolyttmembranen har en tykkelse i området fra 5 til 75 µm.

2. Elektrolysørcelle ifølge krav 1, hvor tykkelsen av polymerelektrolyttmembranen er i området fra 15 til 60 µm.

3. Polymerelektrolyttmembran-vannelektrolysørcellepakke, omfattende flere polymerelektrolyttmembran-vannelektrolysørceller ifølge krav 1 eller 2, forbundet i serie.

4. Polymerelektrolyttmembran-vannelektrolysørsystem, omfattende

et vann- og oksygenhåndteringssystem,

et hydrogenhåndteringssystem,

et vanninntakssystem,

monterings- og emballerings kabinett subsystem;

ventilasjonssystem

kraftelektronikk og kraftforsyning,

systemkontroller og instrumentering

der systemet videre omfatter:

polymerelektrolyttmembran-vannelektrolysørscellepakken ifølge krav 3 og

et tilførsels- og fuktingssystem for fuktet luft.

5. Fremgangsmåte for å fremstille hydrogen i et polymerelektrolyttmembran-vannelektrolysørsystem ifølge krav 4,

der fremgangsmåten omfatter:
påføre elektrisk likestrøm til vannelektrolysørcellen,
tillate vannmolekyler fra katodekammeret å diffundere gjennom polymerelektrolyttmembranen inn i anodekammeret,
oksidere vannmolekyler ved anodekatalysatorlaget til protoner, oksygen og elektroner,
tillate protonene å migrere gjennom polymerelektrolyttmembranen inn i katodekammeret,
redusere protonene ved katodekatalysatorlaget for å produsere hydrogen,
tilføre ionebyttet vann til katodekammeret, og tilføre fuktet luft til anodekammeret.

6. Fremgangsmåte ifølge krav 5, hvor den fuktede luften har en relativ fuktighet (RH) over 75%RH ved en nominell driftstemperatur av elektrolysøren.

7. Fremgangsmåte ifølge krav 5 eller 6, hvor den fuktede luft er overmettet luft.

8. Fremgangsmåte ifølge et hvilket som helst av kravene 5 til 7, hvor tykkelsen av polymerelektrolyttmembranen er i området fra 15 til 60 µm.

Figure 1

State of the art

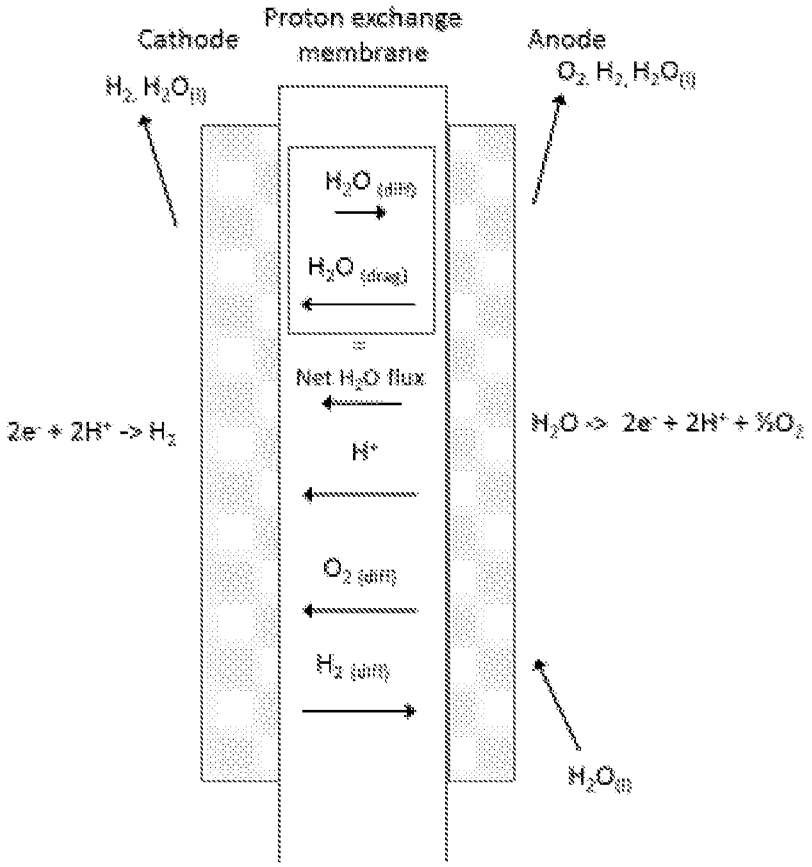


Figure 2

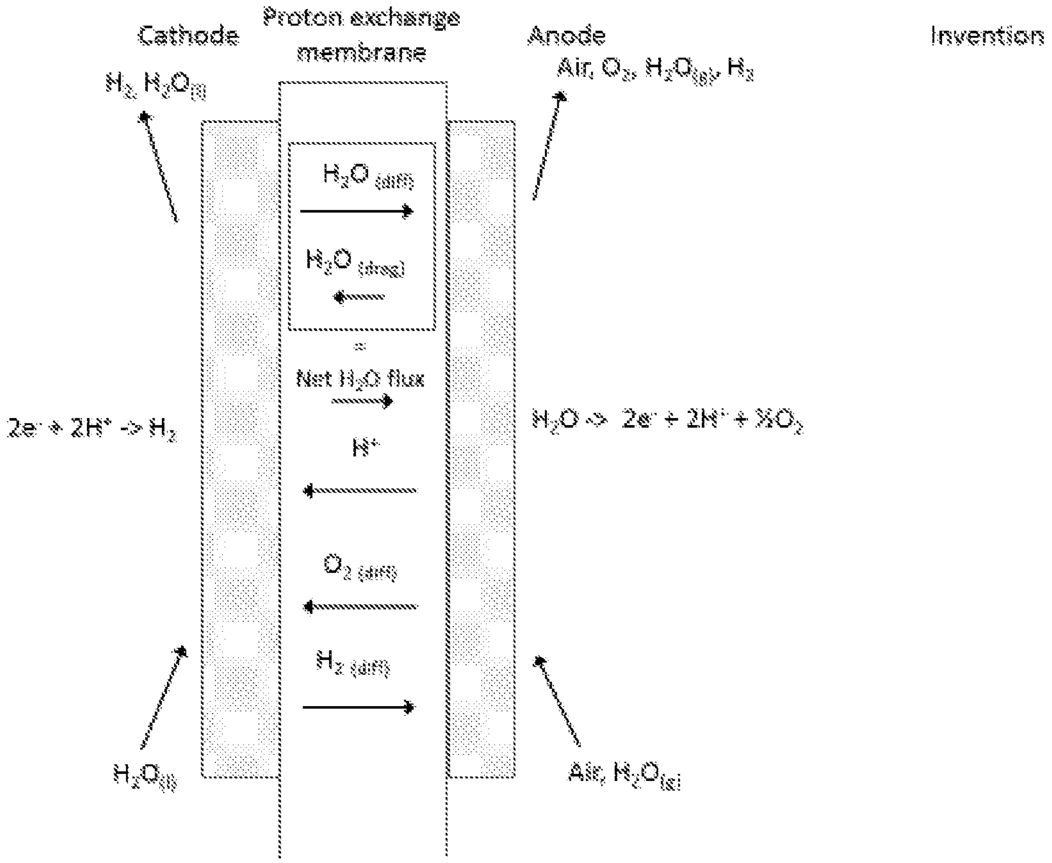
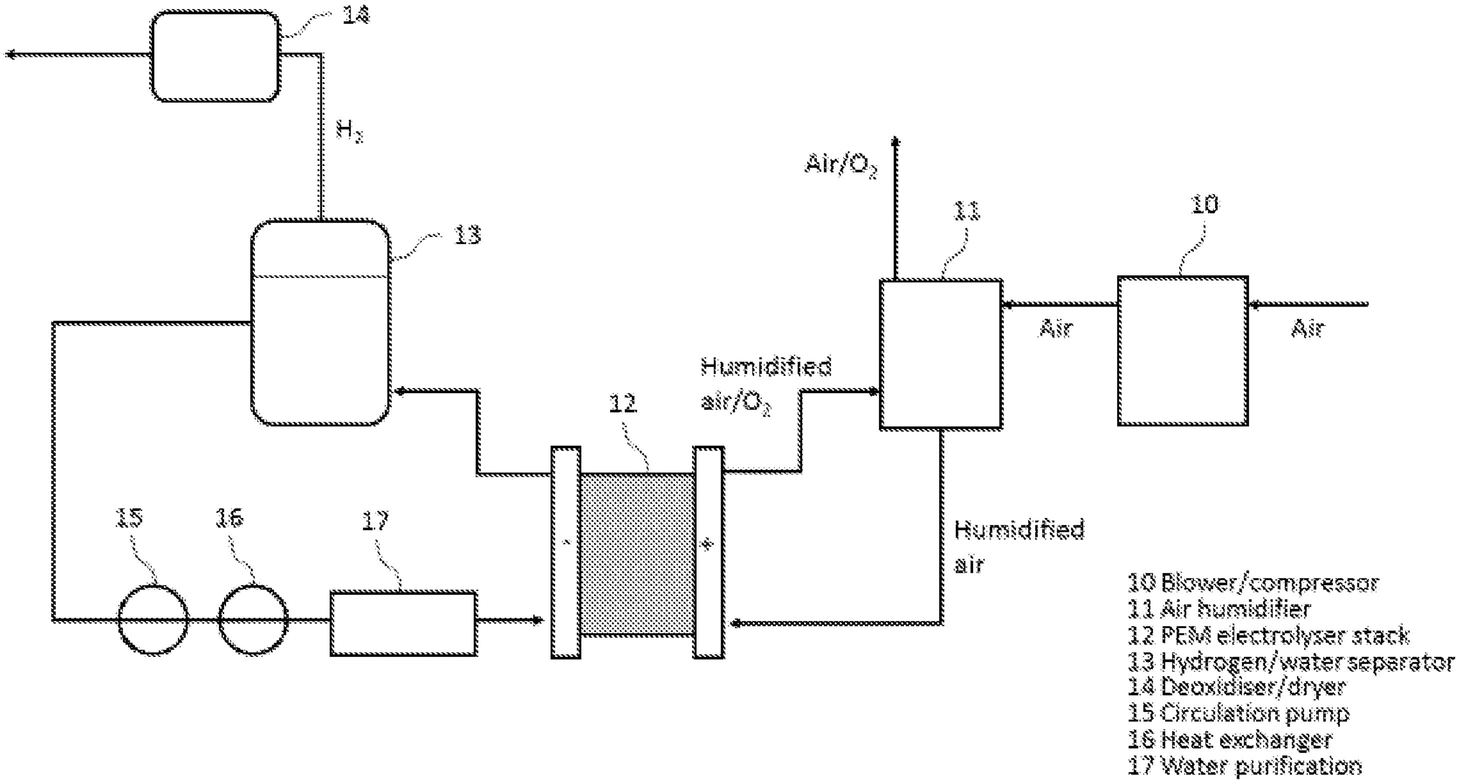
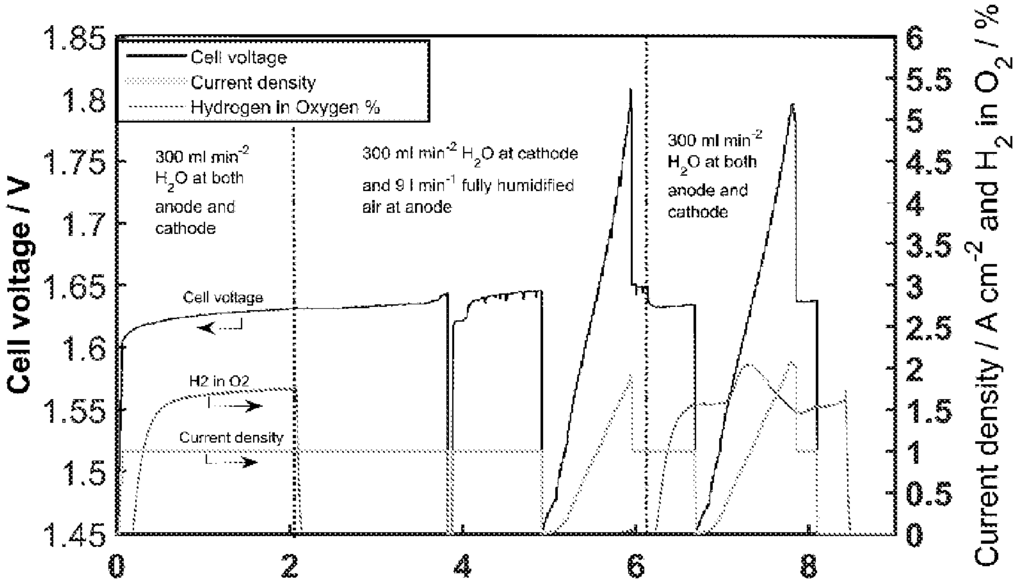

Cathode
Proton exchange membrane
Anode
Invention
H_2, $H_2O_{(l)}$
Air, O_2, $H_2O_{(g)}$, H_2
$H_2O_{(diff)}$
$H_2O_{(drag)}$
=
Net H_2O flux
$2e^- + 2H^+ \rightarrow H_2$
$H_2O \rightarrow 2e^- + 2H^+ + ½O_2$
H^+
$O_{2\,(diff)}$
$H_{2\,(diff)}$
$H_2O_{(l)}$
Air, $H_2O_{(g)}$

Figure 3



10 Blower/compressor
11 Air humidifier
12 PEM electrolyser stack
13 Hydrogen/water separator
14 Deoxidiser/dryer
15 Circulation pump
16 Heat exchanger
17 Water purification

Figure 4


Cell voltage
Current density
Hydrogen in Oxygen %
300 ml min^{-2} H_2O at both anode and cathode
300 ml min^{-2} H_2O at cathode and 9 l min^{-1} fully humidified air at anode
300 ml min^{-2} H_2O at both anode and cathode
Cell voltage
H2 in O2
Current density
Cell voltage / V
1.85
1.8
1.75
1.7
1.65
1.6
1.55
1.5
1.45
0
2
4
6
8
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Current density / A cm^{-2} and H_2 in O_2 / %