

US 20140291162A1

(19) **United States**(12) **Patent Application Publication**  
**Sala et al.**(10) **Pub. No.: US 2014/0291162 A1**(43) **Pub. Date: Oct. 2, 2014**(54) **METHOD AND SYSTEM FOR TREATING  
CARBON GASES BY ELECTROCHEMICAL  
HYDROGENATION IN ORDER TO OBTAIN A  
CXHYOZ COMPOUND****Publication Classification**(51) **Int. Cl.**  
**C25B 3/04** (2006.01)  
(52) **U.S. Cl.**  
CPC ..... **C25B 3/04** (2013.01)  
USPC ..... **205/446; 205/455; 205/450; 205/448;**  
204/262(71) Applicant: **AREVA**, Paris (FR)(72) Inventors: **Béatrice Sala**, Saint Gely Du Fesc (FR);  
**Frédéric Grasset**, Montpellier (FR);  
**Olivier Lacroix**, Montpellier (FR);  
**Abdelkader Sirat**, Montpellier (FR);  
**Elodie Tetard**, Montpellier (FR); **Kamal**  
**Rahmouni**, Montpellier (FR); **Joel**  
**Mazoyer**, Saint-Gilles (FR)(21) Appl. No.: **14/350,837**(22) PCT Filed: **Oct. 11, 2012**(86) PCT No.: **PCT/FR2012/052319**§ 371 (c)(1),  
(2), (4) Date: **Apr. 10, 2014**(30) **Foreign Application Priority Data**

Oct. 12, 2011 (FR) ..... 1159223

(57) **ABSTRACT**

The present invention relates to a method for treating CO<sub>2</sub> by electrochemical hydrogenation, said method comprising: a step of transferring heat from a heating means (160) towards a proton-conductive electrolyser (110) such that said electrolyser (110) reaches an operating temperature suitable for electrolysing steam; a step of feeding the CO<sub>2</sub> produced by said heating means (160) at the cathode of the electrolyser; a step of feeding the steam at the anode; a step of oxidising the steam at the anode; a step of generating protonated species in the membrane with proton conduction; a step of migrating said protonated species into said proton-conductive membrane; a step of reducing said protonated species on the surface of the cathode into reactive hydrogen atoms; and a step of hydrogenating the CO<sub>2</sub> on the surface of the cathode of the electrolyser (110) by means of said reactive hydrogen atoms, said hydrogenation step enabling the formation of C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> compounds, where x≥1; 0<y≤(2x+2) and 0≤z≤2x.

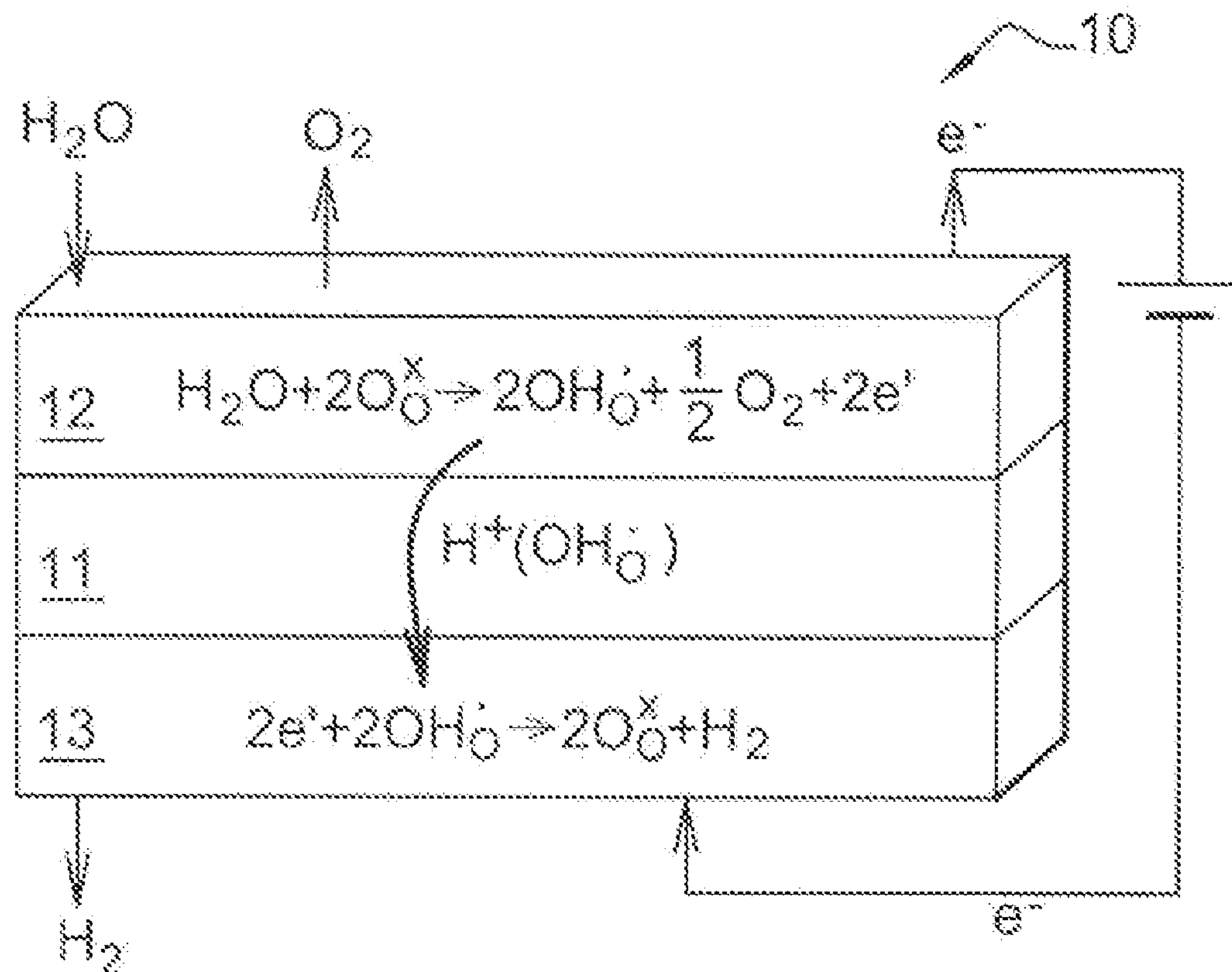


Fig. 1

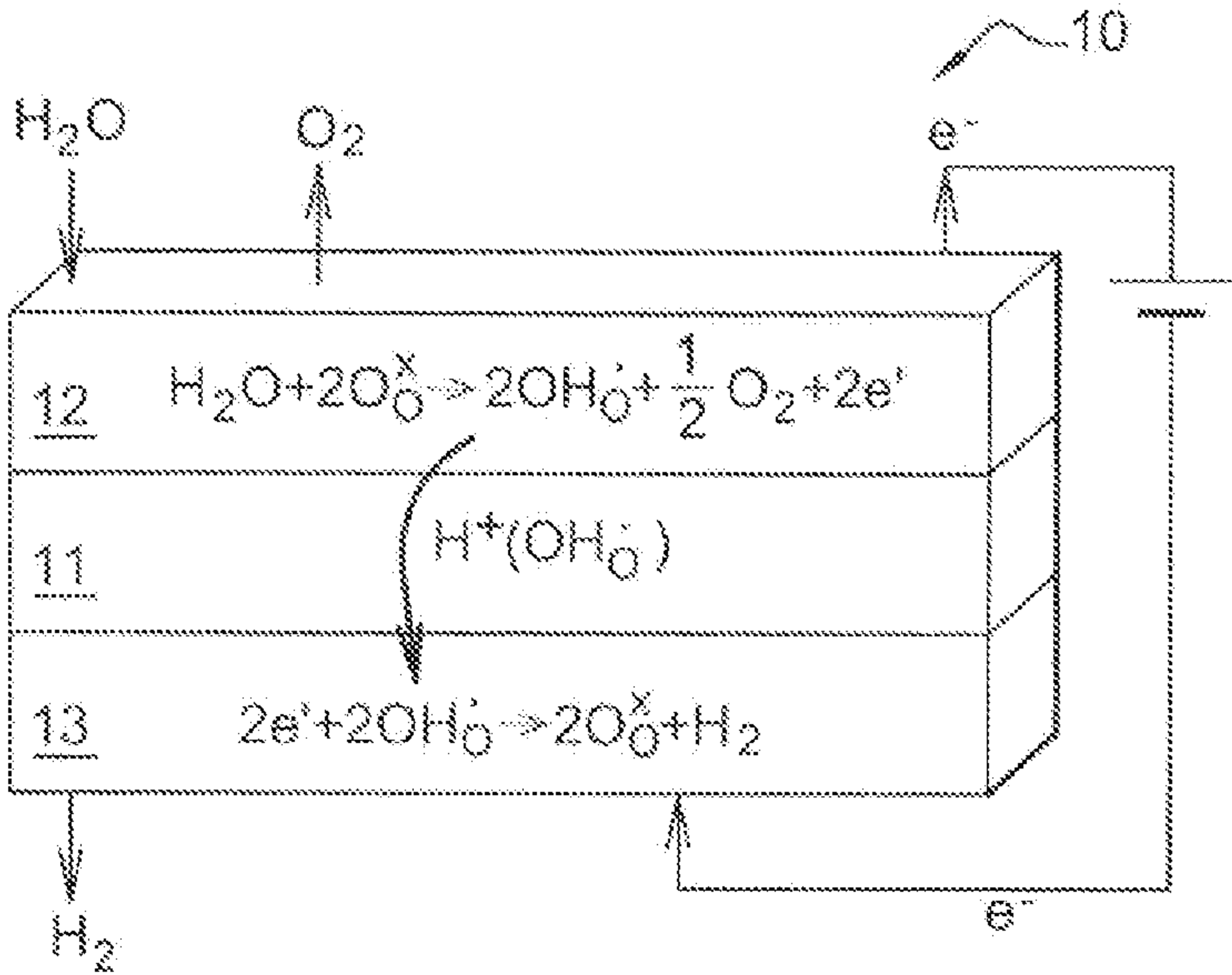
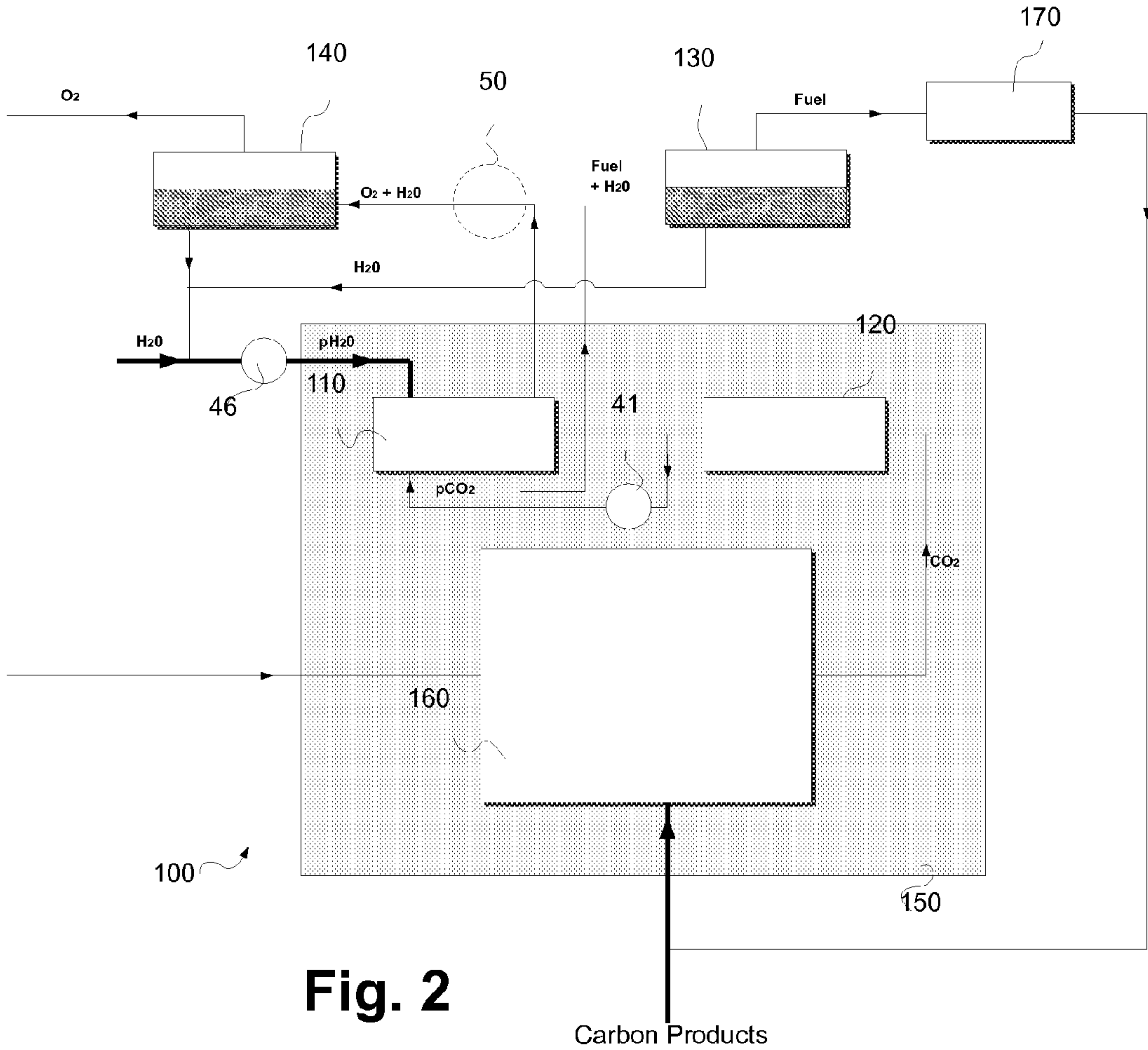
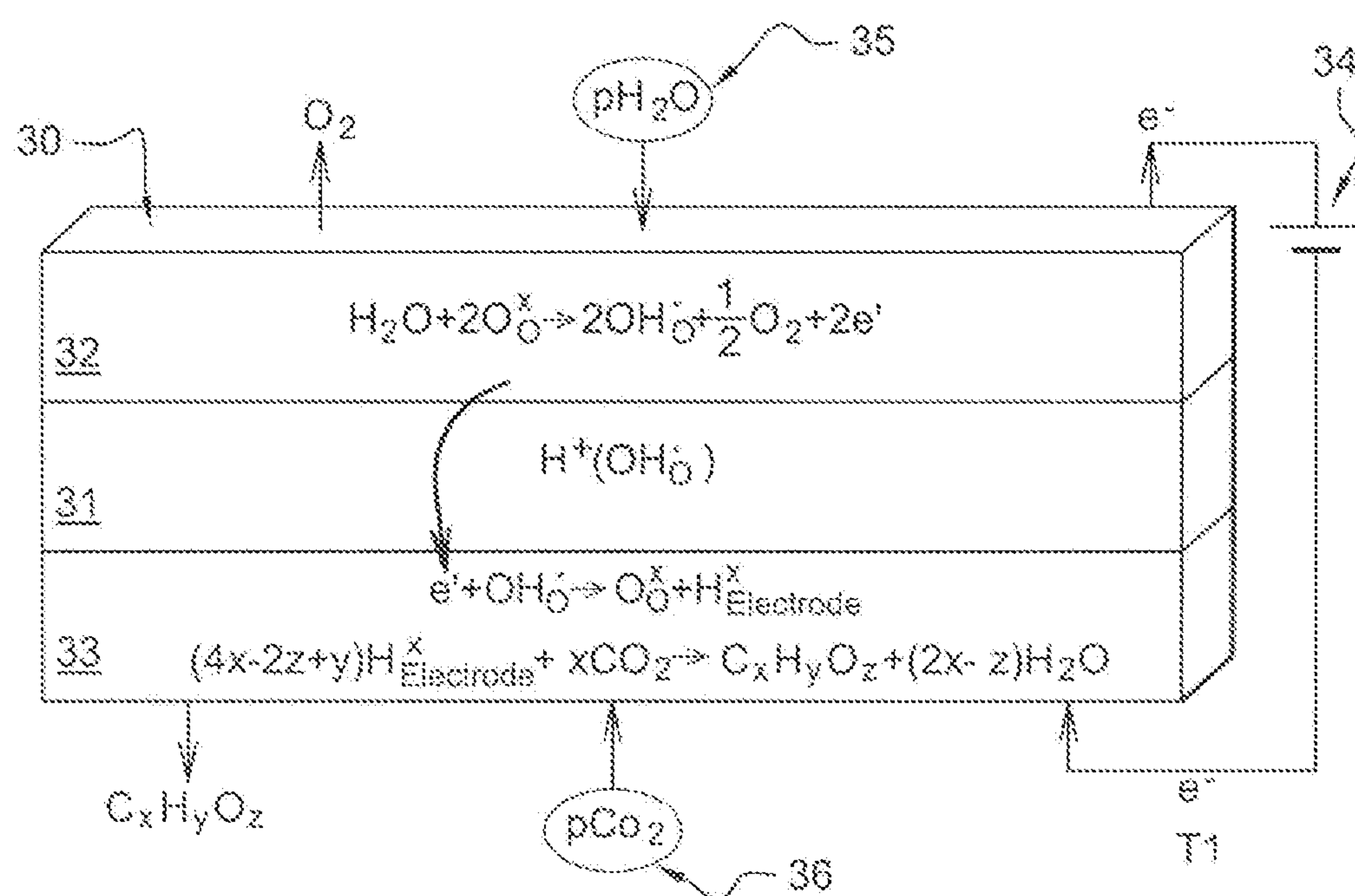


Fig. 2





**Fig. 3**



# METHOD AND SYSTEM FOR TREATING CARBON GASES BY ELECTROCHEMICAL HYDROGENATION IN ORDER TO OBTAIN A CXHYOZ COMPOUND

[0001] The present invention relates to a method and a system for treating carbon gases—carbon dioxide (CO<sub>2</sub>) and/or carbon monoxide (CO)—from very reactive hydrogen generated by electrolysis of water in order to obtain a C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> type compound, particularly where  $x \geq 1$ ;  $0 < y \leq (2x+2)$  and  $0 \leq z \leq 2x$ .

[0002] Conductive ceramic membranes are today the subject of wide-spread research to enhance their performances; notably, said membranes find particularly interesting applications in the fields:

[0003] of the electrolysis of water at high temperature for the production of hydrogen,

[0004] of the treatment of carbon gases (CO<sub>2</sub>, CO) by electrochemical hydrogenation in order to obtain C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> type compounds ( $x \geq 1$ ;  $0 < y \leq (2x+2)$  and  $0 \leq z \leq 2x$ ), the patent application WO2009150352 describes an example of such a method.

[0005] At the present time, two steam electrolysis production methods are known:

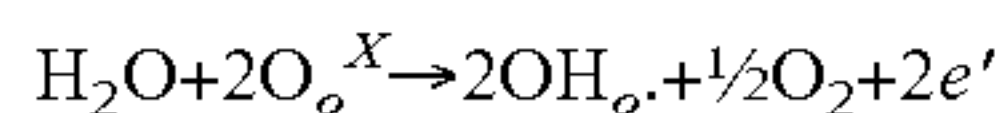
[0006] electrolysis using O<sup>2-</sup> anionic conductors and operating at temperatures generally comprised between 750° C. and 1000° C.;

[0007] electrolysis using the protonic conductors that are involved in this patent.

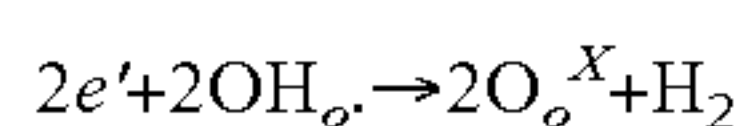
[0008] The production method, illustrated in FIG. 1, uses an electrolyte capable of conducting protons and operating at temperatures generally comprised between 200° C. and 800° C.

[0009] More specifically, this FIG. 1 schematically represents an electrolyser 10 comprising a proton-conducting ceramic membrane 11 assuring the function of electrolyte separating an anode 12 and a cathode 13.

[0010] The application of a potential difference between the anode 12 and the cathode 13 leads to an oxidation of the steam H<sub>2</sub>O on the side of the anode 12. The steam fed into the anode 12 is thus oxidised to form oxygen O<sub>2</sub> and H<sup>+</sup> ions (or OH<sub>o</sub>. in the Kröger-Vink notation), said reaction releasing electrons e<sup>-</sup> according to the equation:

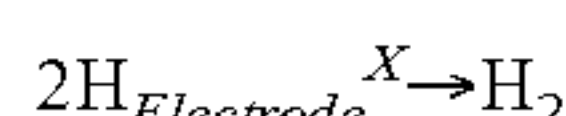


[0011] The H<sup>+</sup> ions (or OH<sub>o</sub>. in the Kröger-Vink notation) migrate through the electrolyte 11, to form hydrogen H<sub>2</sub> on the surface of the cathode 13 according to the equation:



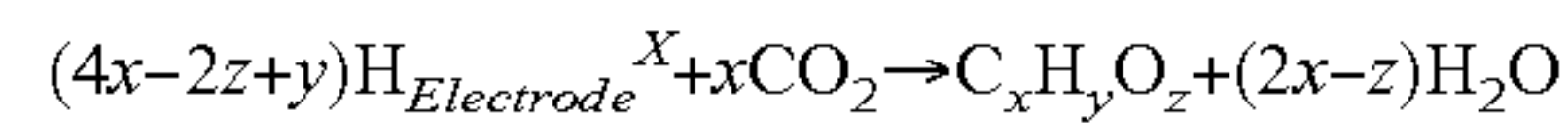
[0012] Thus, this method provides at the outlet of the electrolyser 10 pure hydrogen—cathodic compartment—and oxygen mixed with steam—anodic compartment.

[0013] More specifically, the formation of H<sub>2</sub> goes through the formation of intermediate compounds which are hydrogen atoms adsorbed on the surface of the cathode with variable energies and degrees of interaction and/or radical hydrogen atoms H. (or H<sub>Electrode</sub><sup>X</sup> in the Kröger-Vink notation). These species being highly reactive, they normally recombine to form hydrogen H<sub>2</sub> according to the equation:



[0014] These highly reactive species are used to carry out the treatment of carbon gases (CO<sub>2</sub>, CO) by electrochemical hydrogenation so as to obtain at the outlet of the electrolyser

10 C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> type compounds ( $x \geq 1$ ;  $0 < y \leq (2x+2)$  and  $0 \leq z \leq 2x$ , according to the following relationship:



[0015] The aim of the invention is to reclaim the carbon gases resulting for example from the production of heating from carbon products (coal, wood, oil), or the incineration of waste, and to reduce in an optimal manner the production of greenhouse gases for carrying out the treatment by hydrogenation.

[0016] To this end, the invention proposes a method for treating CO<sub>2</sub> and/or CO by electrochemical hydrogenation in order to obtain a C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> type compound, where  $x \geq 1$ ;  $0 < y \leq (2x+2)$  and  $z$  is comprised between 0 and  $2x$ , said CO<sub>2</sub> and/or CO being obtained by the combustion of carbon products via heating means (160), said method comprising:

[0017] a step of transferring heat from heating means to a proton-conducting electrolyser such that said electrolyser reaches an operating temperature T1 suitable for electrolysing steam, said proton-conducting electrolyser comprising a proton-conducting membrane arranged between an anode and a cathode;

[0018] a step of feeding the CO<sub>2</sub> and/or the CO produced by said heating means at the cathode of the proton-conducting electrolyser;

[0019] a step of feeding the steam at the anode of said electrolyser;

[0020] a step of oxidising steam at the anode;

[0021] a step of generating protonated species in the proton-conducting membrane after said step of oxidation;

[0022] a step of migrating said protonated species in said proton-conducting membrane;

[0023] a step of reducing said protonated species on the surface of the cathode in the form of reactive hydrogen atoms;

[0024] a step of hydrogenating CO<sub>2</sub> and/or CO on the surface of the cathode of the electrolyser by means of said reactive hydrogen atoms, said hydrogenation step making it possible to form C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> type compounds, where  $x \geq 1$ ;  $0 < y \leq (2x+2)$  and  $0 \leq z \leq 2x$ .

[0025] Reactive hydrogen atoms are taken to mean atoms absorbed on the surface of the cathode and/or radical hydrogen atoms H (or H<sub>Electrode</sub><sup>X</sup> in the Kröger-Vink notation).

[0026] Thus, the method according to the invention makes it possible to recycle the carbon gases produced by heating means resulting from the combustion of carbon products by using jointly the electrolysis of steam, which generates highly reactive hydrogen at the cathode of the electrolyser, with an electrocatalysed hydrogenation of the carbon products injected at the cathode of the electrolyser by reaction with highly reactive hydrogen.

[0027] As an example, said C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> type compounds are paraffins C<sub>n</sub>H<sub>2n+2</sub>, olefins C<sub>2n</sub>H<sub>2n</sub>, alcohols C<sub>n</sub>H<sub>2n+2</sub>OH or C<sub>n</sub>H<sub>2n-1</sub>OH, aldehydes and ketones C<sub>n</sub>H<sub>2n</sub>O.

[0028] Advantageously, the C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> compounds produced are compounds making it possible to supply the combustion of heating means so as to reduce the external input of carbon products. Advantageously, the compounds formed are carbon product fuels, such as for example aliphatics or aromatics belonging to the family of alkanes, alkenes or alkynes, substituted or not, being able to include one or more alcohol, aldehyde, ketone, acetal, ether, peroxide, ester, anhydride functions.



[0029] The invention also makes it possible to use advantageously the heat produced by the heating means (resulting from the combustion of carbon products) to heat the proton-conducting electrolyser, the heating of the electrolyser being required to carry out the electrolysis reaction and the electrocatalysed hydrogenation reaction. Thus, the electrolyser does not require the use of specific costly heating means, generating greenhouse gases.

[0030] The method according to the invention may also have one or more of the characteristics below, considered individually or according to any technically possible combinations thereof:

- [0031] the method comprises a step of using the  $C_xH_yO_z$  type compounds produced by hydrogenation as fuel of said heating means;
- [0032] prior to the use of the  $C_xH_yO_z$  type compounds as fuel of said heating means, said method comprises a step of phase separation making it possible to inject into the heating means the  $C_xH_yO_z$  type compounds uniquely in gaseous form;
- [0033] prior to said step of feeding the  $CO_2$  and/or the CO produced by said heating means into the cathodic compartment of the electrolyser, said method comprises a step of purifying the  $CO_2$  and/or the CO produced by said heating means so as to obtain pure  $CO_2$  and/or CO;
- [0034] said step of oxidising the steam at the anode generates oxygen at the outlet of the anodic compartment;
- [0035] said method comprises a step of phase separation of the oxygen produced by said electrolyser,
- [0036] said method comprises a step of re-injecting the oxygen in gaseous form into said heating means;
- [0037] the method comprises a step of controlling the nature of the  $C_xH_yO_z$  type compounds formed as a function of the potential and/or the current applied at the cathode or at the terminals of the electrolyser;
- [0038] the  $C_xH_yO_z$  type compounds formed belong to the family of alkanes or alkenes or alkynes, substituted or not, being able to include one or more alcohol or aldehyde or ketone or acetal or ether or peroxide or ester or anhydride functions;
- [0039] the  $C_xH_yO_z$  type compounds formed are carbon compound fuels;
- [0040] said step of heat transfer from the heating means to said electrolyser is carried out by means of a heat exchanger;
- [0041] said step of heat transfer from the heating means to said electrolyser is carried out by direct heat transfer, said electrolyser being positioned in a heat area in the vicinity of said heating means;
- [0042] the heat transfer from the heating means to a proton-conducting electrolyser is carried out such that said electrolyser reaches a temperature not less than  $200^\circ C.$  and not more than  $800^\circ C.$ , advantageously comprised between  $350^\circ C.$  and  $650^\circ C.$ ;
- [0043] the heat transfer from the heating means to a proton-conducting electrolyser is carried out such that said electrolyser reaches a temperature comprised between  $500^\circ C.$  and  $600^\circ C.$
- [0044] The subject matter of the invention is also a system for treating carbon gases by electrochemical hydrogenation for the implementation of the method according to the invention, said system comprising:
  - [0045] heating means emitting  $CO_2$  and/or CO through the combustion of carbon products;

- [0046] a proton-conducting electrolyser comprising an electrolyte in the form of a proton-conducting membrane, an anode and a cathode; said electrolyser being positioned in the vicinity of the heating means;

- [0047] means for inserting under pressure steam into said electrolyte via said anode;

- [0048] means for feeding under pressure the  $CO_2$  and/or the CO produced by the heating means on the surface of the cathode of the electrolyser;

- [0049] means for evacuating the  $C_xH_yO_z$  type compounds formed by hydrogenation on the surface of the cathode of the electrolyser;

- [0050] means for evacuating the oxygen and the water generated at the anode by the steam electrolysis reaction.

[0051] According to an advantageous embodiment of the invention, the heating means are formed of a boiler.

[0052] Other characteristics and advantages of the invention will become clear from the description that is given thereof below, by way of indication and in no way limiting, with reference to the appended figures, among which:

[0053] FIG. 1, already described, is a simplified schematic representation of a proton-conducting steam electrolyser,

[0054] FIG. 2 is a schematic representation of a system for treating carbon gases produced by a boiler during the combustion of carbon products;

[0055] FIG. 3 is a general simplified schematic representation of an electrolysis cell for the implementation of the method according to the invention.

[0056] FIG. 2 schematically represents a system for treating carbon gases 100 enabling the implementation of the method according to the invention.

[0057] The treatment system 100 comprises:

- [0058] heating means 160, such as a boiler, discharging  $CO_2$  and/or CO as well as other gases resulting from the combustion of carbon products used for the production of heat;

- [0059] a purifier 120 making it possible to purify the gases discharged by the boiler 160 so as to isolate the  $CO_2$  and/or the CO;

- [0060] a proton-conducting electrolyser 110 comprising an electrolyte 31 in the form of a proton-conducting membrane, an anode 32 and a cathode 33 (FIG. 3);

- [0061] means 34 (FIG. 3) for inducing a current circulating between the anode 32 and the cathode 34 of the electrolyser 110;

- [0062] means 41 making it possible to insert, advantageously under pressure, steam  $pH_2O$  into the electrolyte via the anode 32;

- [0063] means 42 for feeding, advantageously under pressure, the  $pCO_2$  and/or the  $pCO$  purified on the surface of the cathode 33 of the electrolyser 110;

- [0064] means for evacuating the  $C_xH_yO_z$  type compounds formed by hydrogenation on the surface of the cathode 33 of the electrolyser 110;

- [0065] means for evacuating the oxygen generated at the anode 32 by the steam electrolysis reaction.

[0066] The means 34 for inducing a current circulating between the anode 32 and the cathode 34 may be a voltage, current generator or a potentiostat (in this case, the cell will also comprise at least one reference cathodic or anodic electrode).

[0067] FIG. 3 illustrated in a more detailed manner an embodiment example of an electrolysis cell 30 of the elec-

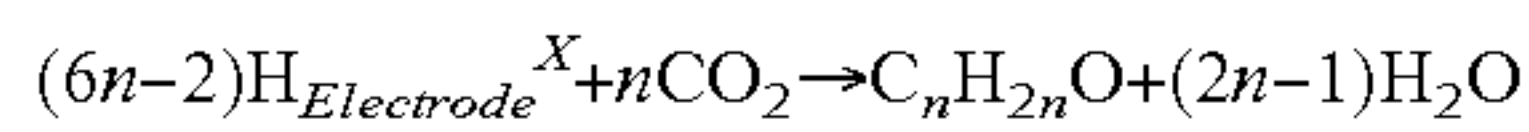
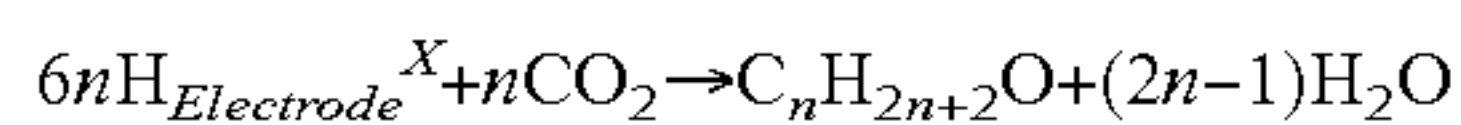
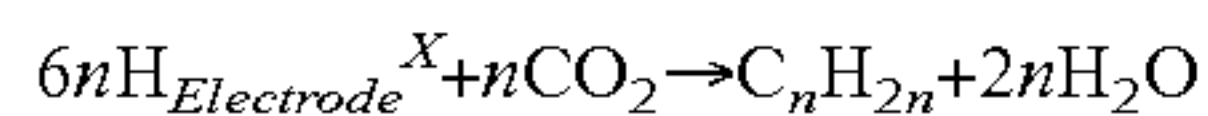


trollyser **110** used to form  $C_xH_yO_z$  type compounds (where  $x \geq 1$ ,  $0 < y \leq (2x+2)$  and  $0 \leq z \leq 2x$ ) after the reduction of the  $CO_2$  and/or the CO.

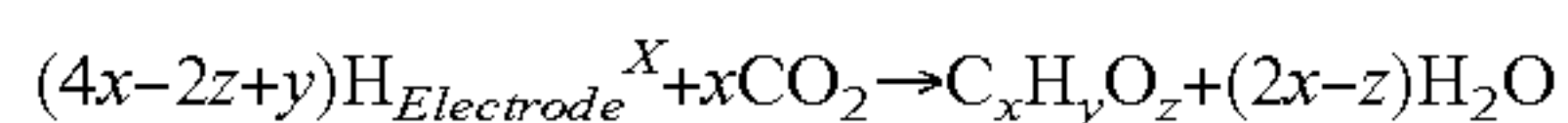
[0068] At the anode **32**, the water is oxidised while releasing electrons while  $H^+$  ions (in  $OH_2$  form) are generated.

[0069] These  $H^+$  ions migrate through the electrolyte **31** and are thus capable of reacting with different compounds that could be injected at the cathode **33**, carbon compounds of  $CO_2$  and/or CO type reacting at the cathode **33** with said  $H^+$  ions to form  $C_xH_yO_z$  type compounds (where  $x \geq 1$ ,  $0 < y \leq (2x+2)$  and  $0 \leq z \leq 2x$ ) and water at the cathode **33**.

[0070] The chemical equations of the different reactions may notably be written:



[0071] The nature of the compound formed depending on the operating conditions, the overall reaction of formation of  $C_xH_yO_z$  may thus be written:



[0072] The nature of the  $C_xH_yO_z$  compounds synthesized at the cathode **33** depends on numerous operating parameters such as, for example, the pressure of the cathodic compartment, the partial pressure of the gases, the operating temperature T1, the couple potential/current/voltage applied at the cathode **33** or at the terminals of the electrolyser, the dwell time of the gas and the nature of the electrodes.

[0073] The operating temperature T1 of the electrolyser is comprised in the range between 200 and 800° C., advantageously between 350° C. and 650° C. The operating temperature T1 in this range of temperature is also going to depend on the nature of the  $C_xH_yO_z$  carbon compounds that it is wished to generate.

[0074] These operating parameters are defined so as to form at the outlet of the cathode **33** of the electrolyser **110** a fuel compound, able to supply the combustion of the boiler **160**.

[0075] It is also advantageous that these operating parameters are defined so as to produce hydrogen at the same time as the  $C_xH_yO_z$  compound. The hydrogen/ $C_xH_yO_z$  compound mixture has the advantage of aiding the combustion of the  $C_xH_yO_z$  compound in the heating means.

[0076] According to an embodiment example, the operating parameters are defined so as to obtain a mixture formed of 90%  $C_xH_yO_z$  compound and 10% hydrogen.

[0077] According to a first embodiment, the anode **32** and the cathode **33** are preferentially formed of a cermet constituted of the mixture of a proton-conducting ceramic and an electron-conducting passivable alloy that is able to form a protective oxide layer so as to protect it in an oxidising environment (i.e. at the anode of an electrolyser). Said passivable alloy is preferentially a metal alloy.

[0078] The passivable alloy comprises for example chromium (and preferentially at least 40% of chromium) so as to have a cermet having the particularly of not oxidising at temperature. The chromium content of the alloy is determined such that the melting point of the alloy is above the sintering temperature of the ceramic. Sintering temperature is

taken to mean the sintering temperature required to sinter the electrolyte membrane so as to make it leak tight to gas.

[0079] The chromium alloy may also comprise a transition metal so as to retain an electron-conducting character of the passive layer. Thus the chromium alloy is an alloy of chromium and one of the following transition metals: cobalt, nickel, iron, titanium, niobium, molybdenum, tantalum, tungsten, etc.

[0080] The ceramic of the anodic and cathodic **32** and **33** electrodes is advantageously the same ceramic as that used by the formation of the electrolytic membrane of the electrolyte **31**.

[0081] According to an advantageous embodiment of the invention, the proton-conducting ceramic used by the formation of the cermet of the electrodes **32** and **33** and the electrolyte **31** is a perovskite of zirconate type of generic formula  $AZrO_3$  being able to be doped advantageously by an element A selected from lanthanides.

[0082] The use of this type of ceramic for the formation of the membrane thus requires the use of a high sintering temperature in order to obtain a sufficient densification to be leak tight to gas. The sintering temperature of the electrolyte **31** is more particularly defined as a function of the nature of the ceramic but also as a function of the desired porosity level. Conventionally, it is estimated that to be leak tight to gas, the electrolyte **31** has to have a porosity level below 6% (or a density above 94%).

[0083] Advantageously, the sintering of the ceramic is carried out under a reducing atmosphere so as to avoid the oxidation of the metal at high temperature, i.e. under an atmosphere of hydrogen ( $H_2$ ) and argon (Ar), or even carbon monoxide (CO) if there is no risk of carburization.

[0084] The electrodes **32** and **33** of the cell **30** are also sintered at a temperature above 1500° C. (according to the example of sintering of a ceramic of zirconate type).

[0085] According to a second embodiment, the anode **32** and the cathode **33** may also be formed of a ceramic material which is a perovskite doped with a lanthanide. The perovskite may be a zirconate of formula  $AZrO_3$ . The zirconate is doped with a lanthanide, which is for example erbium. Moreover, the perovskite doped with lanthanide is doped with a doping element taken from the following group: niobium, tantalum, vanadium, phosphorous, arsenic, antimony, bismuth. These doping elements are chosen to dope the ceramic because they can go from a degree of oxidation equal to 5 to a degree of oxidation of 3, which makes it possible to release oxygen during sintering. More specifically, the doping element is preferably niobium or tantalum. Each electrode may also comprise a metal mixed with the ceramic so as to form a cermet. The ceramic comprises for example between 0.1% and 0.5% by weight of niobium, between 4 and 4.5% by weight of erbium and the remainder zirconate. The fact of doping the ceramic with niobium, tantalum, vanadium, phosphorous, arsenic, antimony or bismuth makes it possible to render the ceramic conductive to electrons. The ceramic is then a ceramic with mixed conduction; in other words, it is conducting both to electrons and protons whereas in the absence of said doping elements, perovskite doped with a lanthanide with a single degree of oxidation is not conducting to electrons. Such a configuration makes it possible to have electrodes made of a material of same nature as the solid electrolyte, which has good conductivity of both protons and electrons, and this is so even when the ceramic is not mixed with a metal (as is the case of the first embodiment).



[0086] The system 100 further comprises a condenser 130 receiving at the inlet the  $C_xH_yO_z$  compound synthesized at the cathode 33 of the electrolyser 110. The condenser 130 makes it possible to separate the  $C_xH_yO_z$  compound in the gaseous state and the water that are produced by the hydrogenation reaction. Thus, the condenser 130 traps the water in liquid form making it possible to obtain at the outlet of the condenser 130 uniquely the synthesized  $C_xH_yO_z$  compound in the gaseous state (carbon compound fuel in the embodiment example illustrated in FIG. 2). The  $C_xH_yO_z$  compound is then injected into the carbon product supply circuit of the boiler 160 after dehydration in a desiccant cartridge 170. The input of the synthesized  $C_xH_yO_z$  compound makes it possible to reduce the specific input of carbon products. The system according to the invention thus makes it possible to operate in semi-closed circuit, the external input of fuel being reduced by the supply of the boiler with synthesized  $C_xH_yO_z$  compound.

[0087] The water recovered in the condenser 130 is then re-injected into the water supply circuit so as to limit external inputs of water.

[0088] In a similar manner to the preceding paragraph, the system 100 also comprises a condenser 140 receiving at the inlet the oxygen produced by electrolysis of steam at the anode 31. The oxygen being mixed with water at the outlet of the electrolyser 110, the condenser 140 makes it possible to separate oxygen from water. The oxygen is then re-injected into the boiler 160 to supply the combustion of the carbon products, and the water is re-injected into the water supply circuit. The oxygen thereby injected makes it possible to carry out an oxycombustion using directly the oxygen coming out of the electrolyser as oxidant instead of air.

[0089] The condensers 130 and 140 also have the function of cooling the compounds entering into the condensers so as to re-inject into the different circuits of the system 100 compounds cooled to a temperature comprised between 80 and 85° C.

[0090] The heating of the electrolyser 110 is carried out by heat transfer from the boiler 160 to the electrolyser 110 such that the electrolyser reaches the temperature T1 not less than 200° C. and not more than 800° C., advantageously comprised between 350° C. and 650° C.

[0091] To obtain hydrogenated organic compounds, the temperature T1 of the electrolyser must be advantageously comprised between 500° C. and 600° C.

[0092] According to a first embodiment example, the heat transfer is achieved by positioning the electrolyser 110 in a heat area 150 around the boiler 160.

[0093] According to a second embodiment example, the heat transfer is achieved by means of a heat exchanger (not represented) making it possible to transfer the thermal energy produced by the boiler to the electrolyser.

[0094] According to a particular non-limiting embodiment, the system further comprises a turbine positioned at the outlet of the electrolyser, and more specifically at the anodic (steam) and/or cathodic outlet of the electrolyser. In FIG. 2, such a turbine is illustrated as an example in dotted line by the reference 50. In this example, the turbine is positioned in the path of the gaseous flux coming out at the anode of the electrolyser. Such a turbine is adapted to generate electricity by the passage of the gaseous flux. According to an advantageous embodiment of the invention, the electricity produced then makes it possible to electrically supply the electrolyser. Thus, this particular embodiment makes it possible to reduce

the electrical consumption of a specific generator to generate a potential difference at the terminals of the electrolyser.

[0095] According to a particular non-limiting embodiment, the system according to the invention comprises thermo-electrical devices advantageously placed so as to recover the heat from the products formed by the water electrolysis reaction.

[0096] According to a particular non-limiting embodiment, the system comprises a heat exchanger adapted to cool the oxygen/water mixture generated at the anode by the electrolysis reaction and to heat the water at the inlet of the electrolyser so as to form steam able to be inserted into the electrolyte via the anode.

[0097] The invention finds a particularly interesting application for reclaiming carbon gases resulting for example from the production of heating from carbon products (coal, wood, oil), or the incineration of wastes.

1. A Method for treating  $CO_2$  and/or CO by electrochemical hydrogenation in order to obtain a  $C_xH_yO_z$  type compound, where  $x \geq 1$ ;  $0 < y \leq (2x+2)$  and  $z$  is comprised between 0 and  $2x$ , said  $CO_2$  and/or CO being obtained by the combustion of carbon products via heating means, said method comprising:

- a step of transferring heat from the heating means to a proton-conducting electrolyser such that said electrolyser reaches an operating temperature (T1) suitable for electrolysing steam, said proton-conducting electrolyser comprising a proton-conducting membrane arranged between an anode and a cathode;
- a step of feeding the  $CO_2$  and/or CO produced by said heating means at the cathode of the proton-conducting electrolyser,
- a step of feeding steam at the anode of said electrolyser;
- a step of oxidising the steam at the anode;
- a step of generating protonated species in the proton-conducting membrane after said step of oxidation;
- a step of migrating said protonated species in said proton-conducting membrane;
- a step of reducing said protonated species on the surface of the cathode in the form of reactive hydrogen atoms;
- a step of hydrogenating  $CO_2$  and/or CO on the surface of the cathode of the electrolyser by means of said reactive hydrogen atoms, said hydrogenation step making it possible to form  $C_xH_yO_z$  type compounds where  $x \geq 1$ ;  $0 < y \leq (2x+2)$  and  $0 \leq z \leq 2x$ .

2. The Method for treating  $CO_2$  and/or CO by electrochemical hydrogenation according to claim 1 wherein said method comprises a step of using  $C_xH_yO_z$  type compounds produced by hydrogenation as fuel for said heating means.

3. The Method for treating  $CO_2$  and/or CO by electrochemical hydrogenation according to claim 1, wherein prior to the use of  $C_xH_yO_z$  type compounds as fuel for said heating means, said method comprises a step of phase separation making it possible to inject into the heating means uniquely gaseous  $C_xH_yO_z$  type compounds:

4. The Method for treating  $CO_2$  and/or CO by electrochemical hydrogenation according to claim 1, wherein prior to said step of introducing the  $CO_2$  and/or the CO produced by said heating means at the cathode of the electrolyser, said method comprises a step of purifying the  $CO_2$  and/or the CO produced by said heating means so as to obtain pure  $CO_2$  and/or CO.



5. The Method for treating CO<sub>2</sub> and/or CO by electrochemical hydrogenation according to claim 1, wherein said step of oxidising the steam at the anode generates oxygen at the outlet of the electrolyser.

6. The Method for treating CO<sub>2</sub> and/or CO by electrochemical hydrogenation according to claim 5 wherein said method comprises a step of phase separation of the oxygen produced by said electrolyser.

7. The Method for treating CO<sub>2</sub> and/or CO by electrochemical hydrogenation according to claim 1, wherein said method comprises a step of re-injecting gaseous oxygen into said heating means.

8. The Method for treating CO<sub>2</sub> and/or CO by electrochemical hydrogenation according to claim 1, wherein the method comprises a step of controlling the nature of the C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> type compounds formed as a function of the potential and/or the current applied at the cathode (33) or at the terminals of the electrolyser.

9. The Method for treating CO<sub>2</sub> and/or CO by electrochemical hydrogenation according to claim 1, wherein the C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> type compounds formed belong to the family of alkanes or alkenes or alkynes, substituted or not, being able to include one or more alcohol or aldehyde or ketone or acetal or ether or peroxide or ester or anhydride functions.

10. The Method for treating CO<sub>2</sub> and/or CO by electrochemical hydrogenation according to claim 1, wherein the C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> type compounds formed are carbon compound fuels.

11. The Method for treating CO<sub>2</sub> and/or CO by electrochemical hydrogenation according to claim 1, wherein said step of heat transfer from the heating means to said electrolyser is carried out by means of a heat exchanger.

12. The Method for treating CO<sub>2</sub> and/or CO by electrochemical hydrogenation according to claim 1, wherein said step of heat transfer from the heating means to said electrolyser is carried out by direct heat transfer, said electrolyser being positioned in a heat area in the vicinity of said heating means.

13. The Method for treating CO<sub>2</sub> and/or CO by electrochemical hydrogenation according to claim 1, wherein said heat transfer from the heating means to a proton-conducting electrolyser is carried out such that said electrolyser reaches a temperature (T1) not less than 200° C. and not more than 800° C., advantageously comprised between 350° C. and 650° C.

14. The Method for treating CO<sub>2</sub> and/or CO by electrochemical hydrogenation according to claim 1, wherein said heat transfer from the heating means to a proton-conducting electrolyser is carried out such that said electrolyser reaches a temperature (T1) comprised between 500° C. and 600° C.

15. A System for treating carbon gases by electrochemical hydrogenation for the implementation of the method according to claim 1, said system comprising:

heating means emitting CO<sub>2</sub> and/or CO through the combustion of carbon products;

a proton-conducting electrolyser comprising an electrolyte in the form of a proton-conducting membrane, an anode and a cathode; said electrolyser being positioned in the vicinity of the heating means;

means for inserting under pressure steam into said electrolyte via said anode;

means for feeding under pressure the CO<sub>2</sub> and/or the CO produced by the heating means on the surface of the cathode of the electrolyser;

means for evacuating the C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> type compounds formed by hydrogenation on the surface of the cathode of the electrolyser;

means for evacuating the oxygen and water generated at the anode by the steam electrolysis reaction.

16. The System for treating carbon gases by electrochemical hydrogenation according to claim 15 wherein the heating means are formed of a boiler.

\* \* \* \* \*