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(54) **PROCESS FOR PRODUCING COMPOUNDS OF THE CXHYOZ TYPE BY REDUCTION OF CARBON DIOXIDE (CO₂) AND/OR CARBON MONOXIDE (CO)**

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(57) **ABSTRACT**

The present invention relates to a process for electrolysing steam introduced under pressure into an anode in compartment (32) of an electrolyser (30) provided with a proton-conducting membrane (31) made of a material that allows protonated species to be incorporated into this membrane under steam, water injected in steam form being oxidized at the anode (32) so as to generate protonated species in the membrane that migrate within this same membrane and are reduced at the surface of the cathode (33) in the form of reactive hydrogen atoms capable of reducing carbon dioxide and/or carbon monoxide, said process comprising the following steps: injection of CO₂ and/or CO under pressure into the cathode compartment (33) of the electrolyser (30); -reduction of the CO₂ and/or CO injected into the cathode compartment (33) by said reactive hydrogen atoms generated, in such a way that the CO₂ and/or the CO form compounds of the C_xH_yO_z type where x>1, y is between 0 and 2x+2 and z is between 0 and 2x.

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Fig. 1

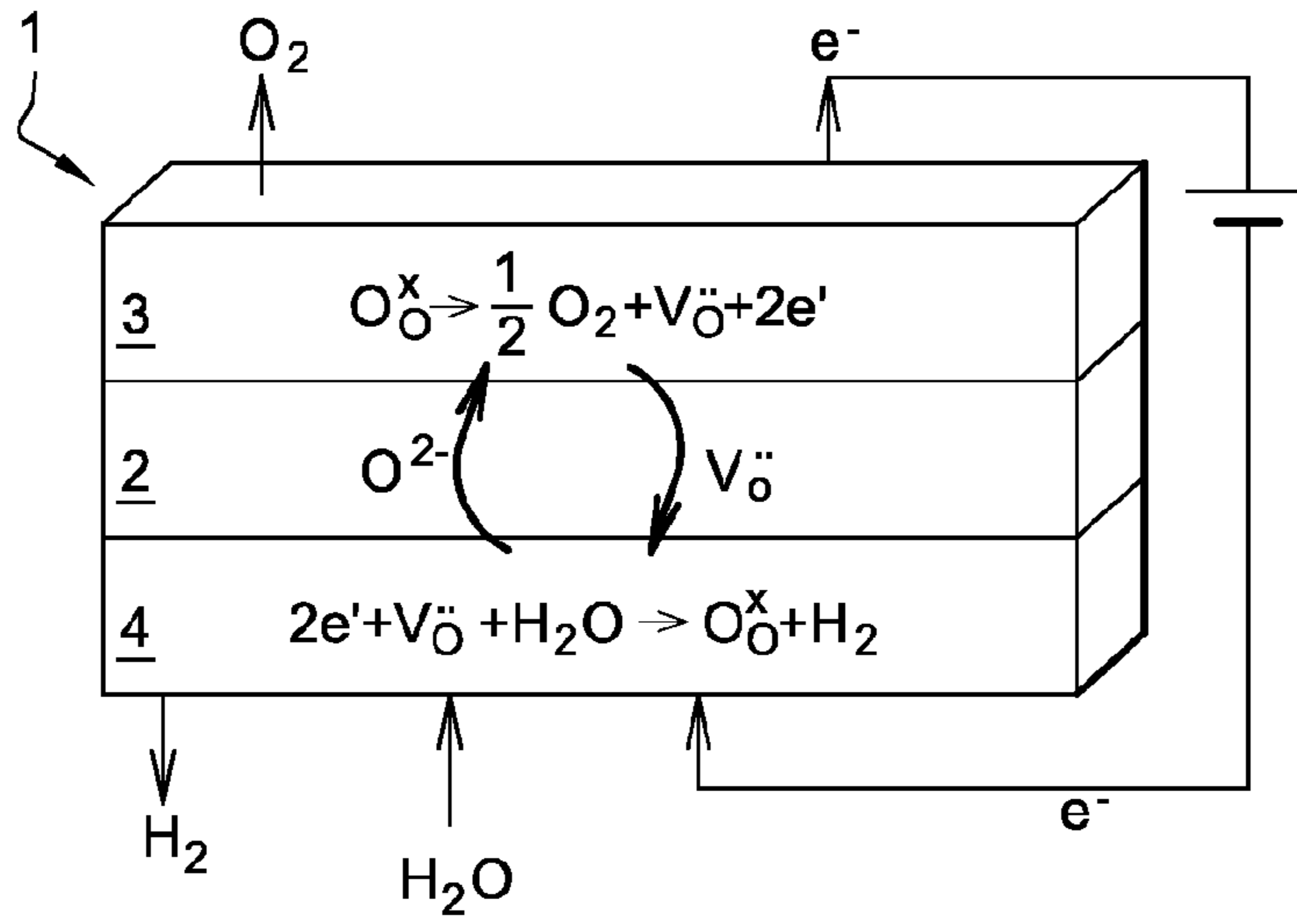


Fig. 2

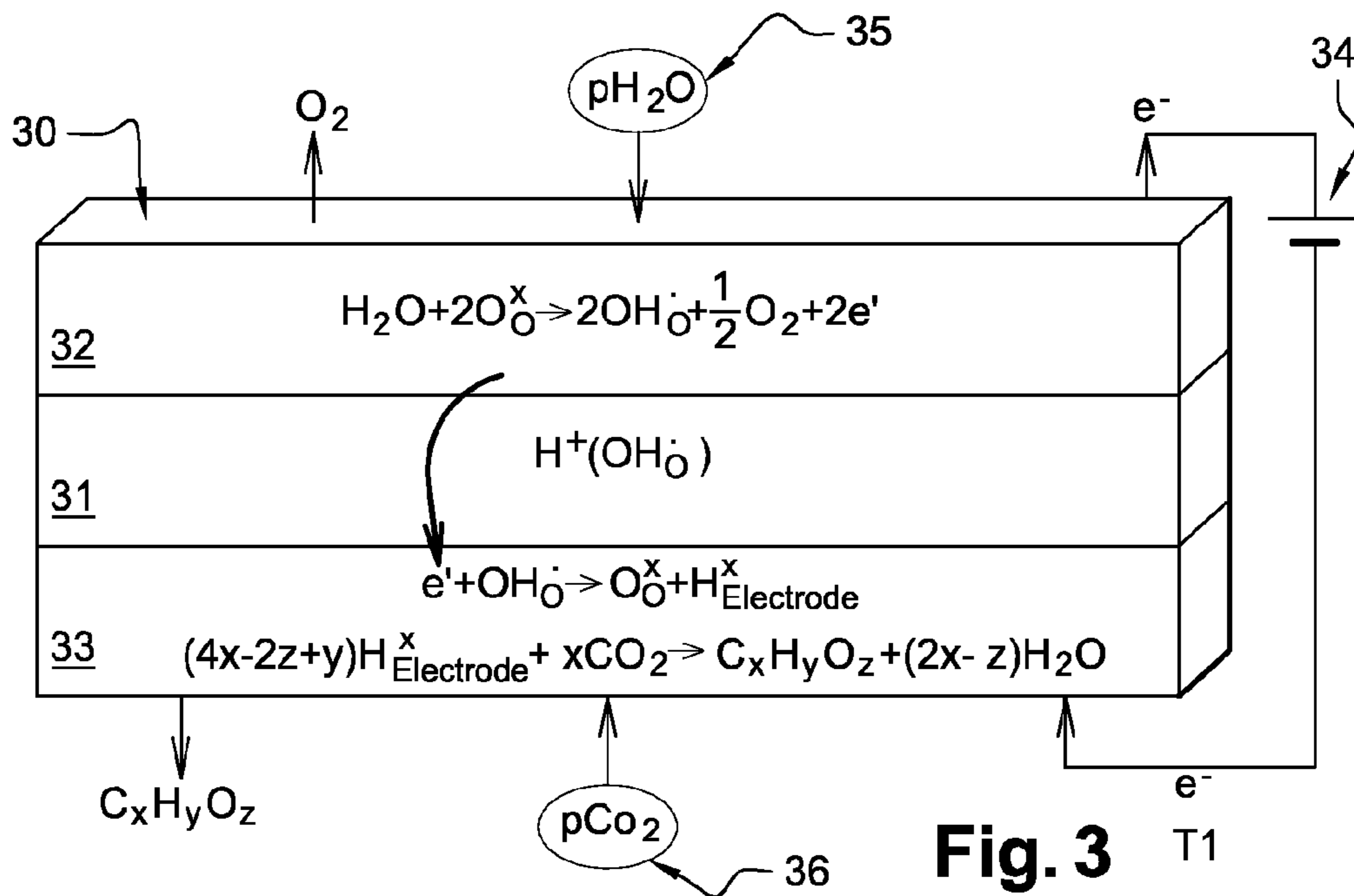
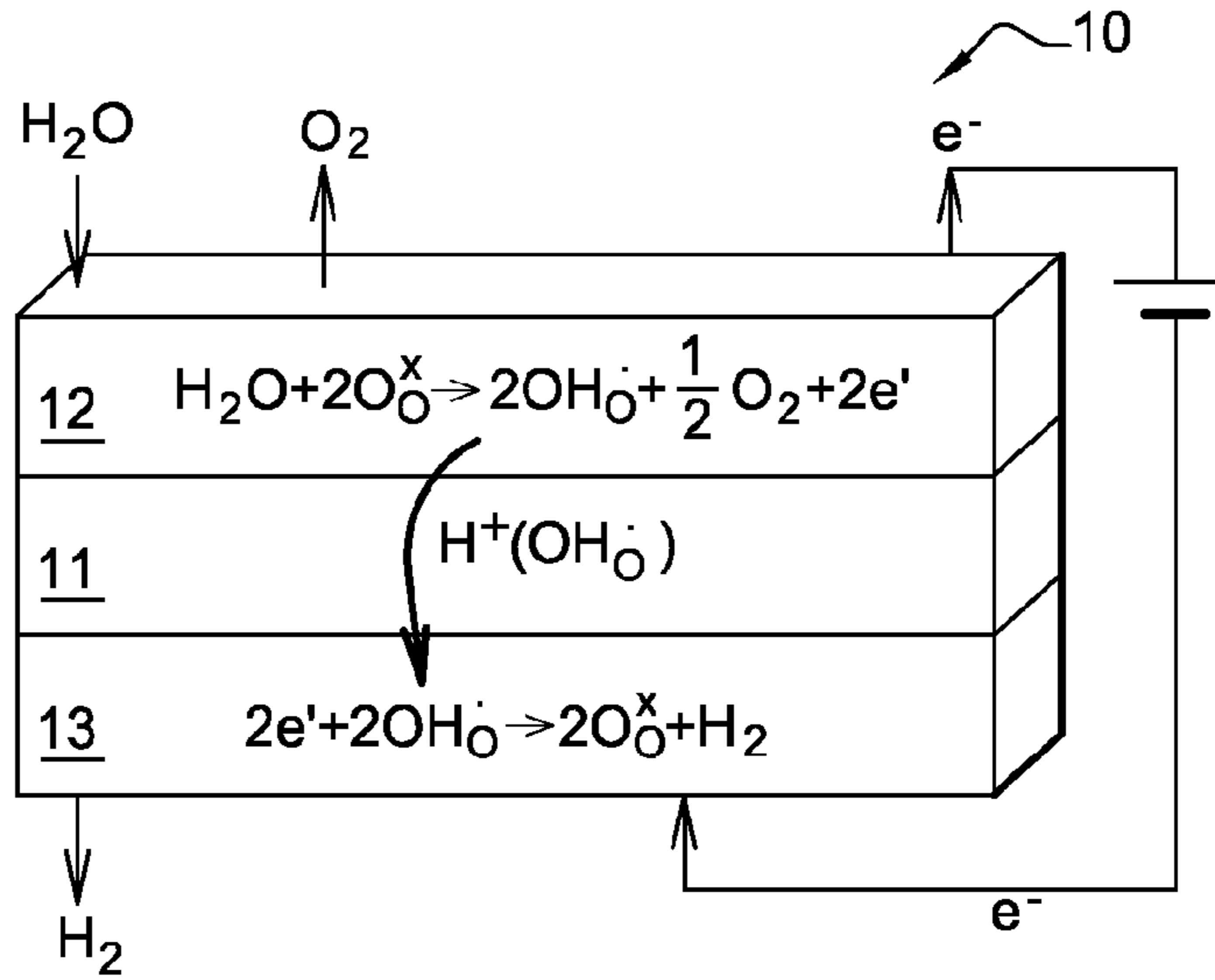


Fig. 3

**PROCESS FOR PRODUCING COMPOUNDS
OF THE CXHYOZ TYPE BY REDUCTION OF
CARBON DIOXIDE (CO₂) AND/OR CARBON
MONOXIDE (CO)**

[0001] The present invention relates to a process for producing compounds of the C_xH_yO_z type, particularly with x>1; y is between 0 and 2x+2 and z is between 0 and 2x, by reduction of carbon dioxide (CO₂) and/or carbon monoxide (CO), particularly from very reactive hydrogen species generated by water electrolysis.

[0002] Today ceramic conducting membranes are the subject of much research to increase their performance; these membranes find particularly interesting applications, among others, in the fields of:

[0003] water electrolysis at high temperature for producing hydrogen,

[0004] in the treatment of carbon-containing gas (CO₂, CO) by electrochemical hydrogenation to obtain compounds of the C_xH_yO_z type (x>1; y is between 0 and 2x+2 and z is between 0 and 2x).

[0005] Today hydrogen (H₂) appears to be a very interesting energy carrier, that is called upon to take on more and more importance to treat, among other substances, petroleum, oils and lubricants, and that may, in the end, be advantageously substituted for petroleum and fossil energies, whose reserves are going to sharply decrease in the decades to come. However, in this perspective, it is necessary to develop effective hydrogen production processes.

[0006] Admittedly, many hydrogen production processes have been described from various sources, but a number of these processes have proved to be unsuitable for the massive industrial production of hydrogen.

[0007] In this context, one may, for example, cite the synthesis of hydrogen from steam reforming hydrocarbons. One of the main problems with this synthetic pathway is that it produces, as by-products, significant quantities of CO₂-type greenhouse gases. In fact, 8 to 10 tons of CO₂ are released to produce 1 ton of hydrogen.

[0008] Therefore two challenges are presented for future years: To search for a new energy carrier that is usable without danger to our environment such as hydrogen, and to reduce the quantity of carbon dioxide.

[0009] The techno-economic valuations of industrial processes now take the latter data into account. However, it is essentially sequestration, in particular underground sequestration in crevices that do not necessarily correspond to old oil deposits, which in the end cannot be without danger.

[0010] It would seem wise to recycle this carbon dioxide in the form of compounds usable in the chemistry field or in the energy production field. The energy necessary for this transformation would be electricity, for example of nuclear origin, and in particular that from reactors such as HTR "High Temperature Reactor" type nuclear reactors or EPR (registered trademark) European pressurized water reactors.

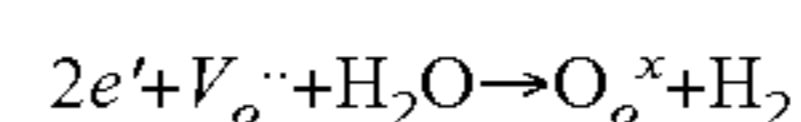
[0011] A promising path for industrial hydrogen production is the technique known as steam electrolysis, for example at high temperature (EHT), at medium temperature, typically over 200° C., or even at an intermediate temperature of between 200° C. and 1000° C.

[0012] Two steam electrolysis production processes are presently known:

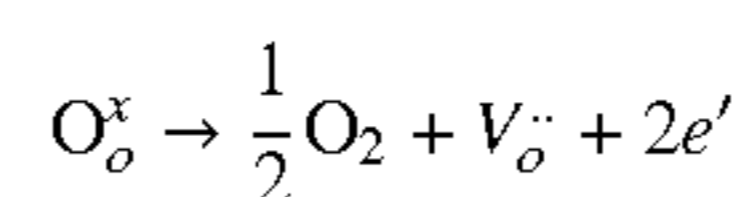
[0013] According to a first process illustrated in FIG. 1, an electrolyte capable of carrying O²⁻ ions and operating at temperatures that are generally between 750° C. and 1000° C. is utilized.

[0014] More precisely, FIG. 1 schematically represents an electrolyser **1** comprising a ceramic membrane **2**, conductor of O²⁻ ions, ensuring the electrolyte function separating an anode **3** and a cathode **4**.

[0015] The application of a potential difference between anode **3** and cathode **4** leads to a reduction in H₂O steam from the cathode **4** side. This reduction forms hydrogen H₂ and ions O²⁻ (O_o^x in Kroger-Vink notation) at the surface of the cathode **4** according to the reaction:



[0016] The O²⁻ ions, more precisely the oxygen vacancies (V_o^{··}), migrate through electrolyte **2** to form oxygen O₂ at the surface of anode **3**, electrons e being released according to the oxidation reaction:

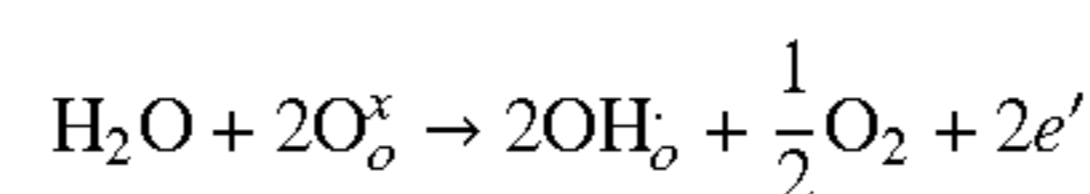


[0017] Thus, the first process enables, from the output of the electrolyzer **1**, oxygen—anode compartment—and hydrogen mixed with steam—cathode compartment—to be generated.

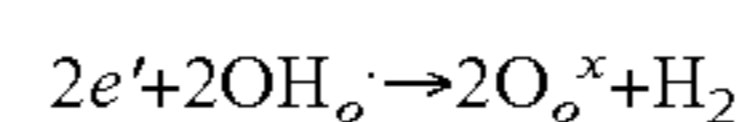
[0018] According to a second process illustrated in FIG. 2, an electrolyte capable of carrying the protons and operating at lower temperatures than those required for the first process described above, generally between 200° C. and 800° C., is utilized.

[0019] More precisely, this FIG. 2 schematically represents an electrolyzer **10** comprising a proton-conducting ceramic membrane **11** ensuring the electrolyte function separating an anode **12** and a cathode **13**.

[0020] The application of a potential difference between anode **12** and cathode **13** leads to oxidation of the H₂O steam from the anode side **12**. The steam injected in anode **12** is thus oxidized to form oxygen O₂ and H⁺ ions (or OH_o[·] in Kroger-Vink notation), this reaction releasing electrons e—according to the equation:



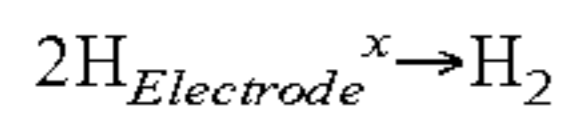
[0021] The H⁺ ions (or OH_o[·] Kroger-Vink notation) migrate through the electrolyte **11** to form hydrogen H₂ at the surface of cathode **13** according to the equation:



[0022] Thus, this process provides, from the output of electrolyzer **10**, pure hydrogen—cathode compartment—and oxygen mixed with steam—anode compartment.

[0023] More precisely, the formation of H₂ passes by the formation of intermediate compounds that are hydrogen atoms adsorbed at the surface of the cathode with variable energies and degrees of interaction and/or radical hydrogen atoms H[·] (or H_{Electrode}^x in Kroger-Vink notation). As these

species are highly reactive, they usually recombine to form hydrogen H_2 according to the equation:



[0024] The present invention aims to reduce the quantity of existing carbon dioxide, for example by recycling this carbon dioxide in the form of compounds usable in the chemistry field or in the energy production field.

[0025] For this purpose, the invention proposes a process for electrolyzing water steam injected under pressure into an anode compartment of an electrolyzer provided with a proton-conducting membrane made of a material enabling protonated species to be incorporated into this membrane under steam, oxidation of the water injected in steam form taking place at the anode so as to generate protonated species in the membrane that migrate within this same membrane and are reduced at the surface of the cathode in the form of reactive hydrogen atoms capable of reducing carbon dioxide CO_2 and/or carbon monoxide CO , said process comprising the following steps:

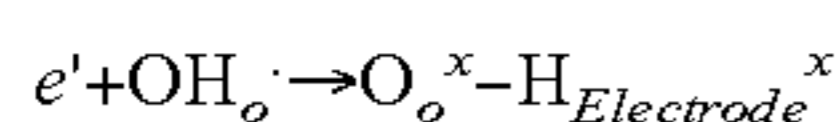
[0026] injection of CO_2 and/or CO under pressure into the cathode compartment of the electrolyzer,

[0027] the reduction of the CO_2 and/or CO injected into the cathode compartment by said reactive hydrogen atoms generated such that the CO_2 and/or the CO form compounds of the $C_xH_yO_z$ type, with $x > 1$; y is between 0 and $2x+2$ and z is between 0 and $2x$.

[0028] As explained above, reactive hydrogen atoms is understood to refer to hydrogen atoms adsorbed at the surface of the cathode with variable energies and degrees of interaction and/or radical hydrogen atoms H^\cdot (or $H_{Electrode}^x$ in Kroger-Vink notation).

[0029] The invention results from the observation that the second process described above generates highly reactive hydrogen at the electrolyzer cathode (particularly hydrogen atoms adsorbed at the surface of the electrode and/or radical hydrogen atoms).

[0030] These highly reactive hydrogen atoms $H_{Electrode}^x$ are formed at the surface of the cathode according to the reaction:



[0031] In fact, in the presence of CO_2 and/or CO on the cathode side, the highly reactive hydrogen $H_{Electrode}^x$ reacts with the carbon compounds on the electrode to give reduced carbon dioxide and/or carbon monoxide compounds of the $C_xH_yO_z$ type with $x > 1$; y is between 0 and $2x+2$ and z is between 0 and $2x$.

[0032] By way of example, these compounds are paraffins C_nH_{2n+2} , olefins $C_{2n}H_{2n}$, alcohols $C_nH_{2n+2}OH$ or $C_nH_{2n-1}OH$, aldehydes and ketones $C_nH_{2n}O$, acids $C_{n-1}H_{2n+1}$ with $n > 1$.

[0033] The invention thus enables steam to be electrolyzed with the joint carbon dioxide and/or carbon monoxide electroreduction as described subsequently.

[0034] The process according to the invention may also present one or more of the characteristics below, considered individually or according to all technically possible combinations:

[0035] the process comprises a step of controlling the nature of the $C_xH_yO_z$ type compounds, formed according to the voltage-current pair applied to the cathode;

[0036] the process comprises a step of utilizing a proton-conducting membrane that is impermeable to the diffu-

sion of oxygen O_2 and H_2 allowing the injection of protonated species into the membrane under steam pressure;

[0037] the process comprises a step of utilizing a proton-conducting membrane of the type: perovskite vacancies, non-stoichiometric perovskites and/or perovskites doped with general formula ABO_3 , of fluorite, pyrochlore $A_2B_2X_7$, apatite $Me_{10}(XO_4)_6Y_2$, oxyapatite $Me_{10}(XO_4)_6O_2$ structure, of hydroxylapatite $Me_{10}(XO_4)_6(OH)_2$ structure, of silicate, aluminosilicate (phyllosilicate or zeolite) structure, silicates grafted with oxyacids or silicates grafted with phosphates;

[0038] the process comprises a step of utilizing an electrolyte supported by the cathode or by the anode so as to reduce its thickness in order to increase its mechanical strength;

[0039] the process comprises a step of utilizing relative partial steam pressure greater than or equal to 1 bar and less than or equal to a burst pressure of the assembly, the latter being greater than or equal to at least 100 bars;

[0040] the relative partial steam pressure is advantageously greater than or equal to 50 bars;

[0041] the relative pressure of CO_2 and/or CO is greater than or equal to 1 bar and less than or equal to a burst pressure of the assembly, the latter being greater than or equal to at least 100 bars;

[0042] the electrolysis temperature is greater than or equal to $200^\circ C.$ and less than or equal to $800^\circ C.$, advantageously between $350^\circ C.$ and $650^\circ C.$;

[0043] the electrodes, of porous structure, are either of ceramic-metal materials or "ceramic" electrodes of mixed electronic and ionic conduction;

[0044] the ceramic-metal materials are, for the cathodes, ceramics compatible with the electrolyte in which the nature of the metal dispersed is advantageously a metal and or a metal alloy, among which one may cite metals such as cobalt, copper, molybdenum, silver, iron, zinc, noble metals (gold, platinum, palladium) and/or transition elements;

[0045] the ceramic-metal materials are, for the anodes, ceramics compatibles with the electrolyte in which the nature of the metal dispersed is advantageously a metal alloy or a passivable metal.

[0046] The invention also relates to a steam electrolysis device for electrolyzing water steam introduced under pressure into an anode compartment of an electrolyzer provided with a proton-conducting membrane, made of a material enabling the injection of protonated species into this membrane under steam after oxidation, comprising:

[0047] an electrolyte in the form of an ion conducting membrane made in said material enabling the injection of protonated species under the effect of the water pressure in said membrane,

[0048] an anode,

[0049] a cathode,

[0050] a generator enabling current to be generated and to apply a potential difference between said anode and said cathode,

characterized in that the generator comprises:

[0051] means for the insertion of steam under pressure in said electrolyte via said anode;

[0052] means to inject CO_2 and/or CO under pressure into the cathode compartment of the electrolyzer, and

[0053] means to reduce the CO₂ and/or the CO introduced into the cathode compartment according to a process in conformance with one of the previous embodiments.

[0054] The device according to the invention may also present one or more of the characteristics below, considered individually or according to all technically possible combinations:

[0055] the material enabling the injection of protonated species is impermeable to O₂ and H₂ gases;

[0056] the material enabling the injection of protonated species has a densification level of over 88%, preferably equal to at least 94%;

[0057] the material enabling the injection of protonated species is an oxygen atom-defective oxide such as an oxygen-defective perovskite acting as a proton conductor; In this case, the oxygen atom-defective oxide may present stoichiometric intervals and/or may be doped.

[0058] Other characteristics and advantages of the invention will clearly emerge from the description given below, for indicative and in no way limiting purposes, with reference to the attached figures, among which:

[0059] FIGS. 1 and 2, already described, are simplified schematic representations of steam, and

[0060] FIG. 3 is a simplified schematic representation of a steam electrolyser performing joint CO₂ and/or CO electroreduction.

[0061] FIG. 3 schematically and in a simplified manner represents an embodiment of an electrolysis device for the production of hydrogen implementing the joint CO₂ and/or CO electroreduction process according to the invention.

[0062] This electrolysis device has a structure similar to that of the device from FIG. 2. Thus, it comprises:

[0063] an anode 32,

[0064] a cathode 33,

[0065] an electrolyte 31,

[0066] a generator 34 ensuring a potential difference between the anode 32 and the cathode 33,

[0067] means 35 enabling the insertion under pressure of steam pH₂O into membrane 31 via cathode 33 (the relative partial steam pressure is greater than or equal to 1 bar and less than or equal to a burst pressure of the assembly, this latter being greater than or equal to at least 100 bars).

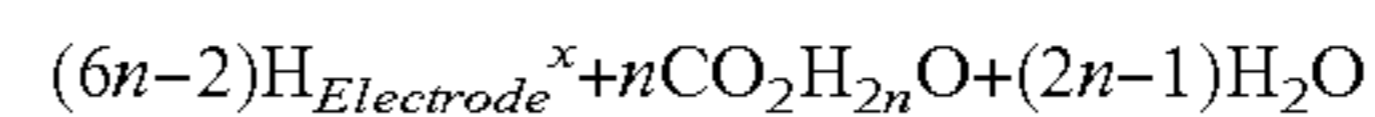
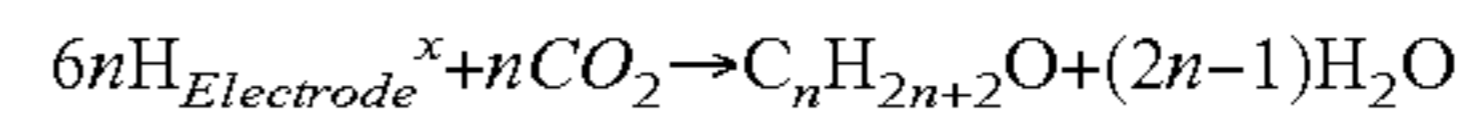
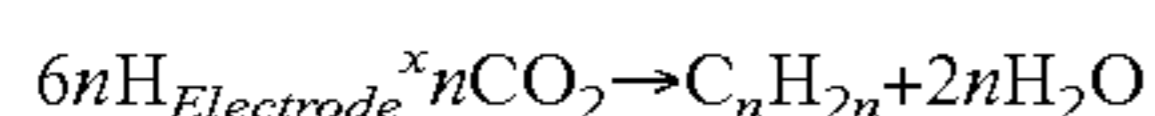
[0068] In conformance with the invention, the device also comprises means 36 enabling the insertion under pressure of gas (pCO₂ and/or CO) into the cathode compartment 33.

[0069] The injection of steam is done via means 35 at the level of anode 32 while the injection of gas CO₂ and/or CO is done via means 36 at the level of cathode 33.

[0070] At anode 32, the water is oxidized by releasing electrons while H⁺ ions (in OH_o⁻ form) are generated according to a process that is similar to the process described with the help of FIG. 2.

[0071] These H⁺ ions migrate through the electrolyte 31, carbon compounds of the CO₂ and/or CO type react at cathode 33 with these H⁺ ions to form compounds of the C_xH_yO_z type (with x>1; y is between 0 and 2x+2 and z is between 0 and 2x) and water at the cathode.

[0072] In particular, the chemical equations of the various reactions may be written as:



[0073] As the nature of the compound formed depends on the process conditions, the overall C_xH_yO_z formation reaction may thus be written as:



[0074] The nature of the C_xH_yO_z compounds synthesized at the cathode depends on many process parameters such as, for example, gas pressure, operating temperature T1 and the voltage-current pair applied to the cathode as described below:

[0075] Concerning the gas pressure, the relative pressure of CO₂ and/or CO is greater than or equal to 1 bar and less than or equal to a burst pressure of the assembly, the latter being greater than or equal to at least 100 bars.

[0076] It will be noted that here the term relative pressure designates the pressure of insertion with relation to atmospheric pressure.

[0077] It will be noted that it is possible to use either a gas stream containing only steam or a gas stream partially containing steam. Thus, depending on the case, the term "partial pressure" will designate either the total pressure of the gas stream in the case where the latter is only constituted of steam or the partial pressure of the steam in the case where the gas stream comprises gases other than steam.

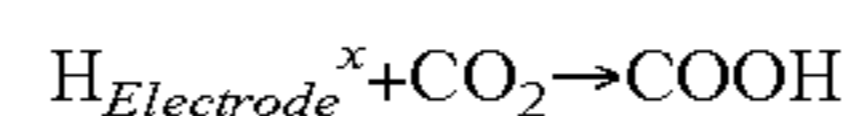
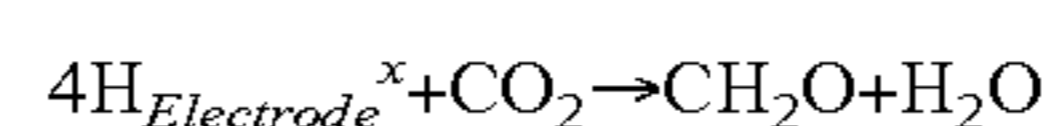
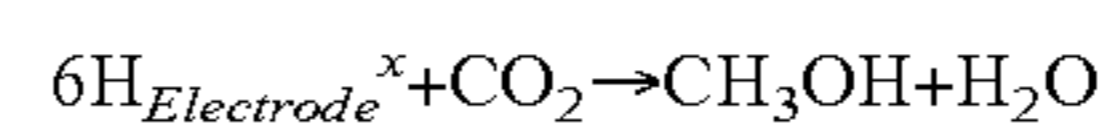
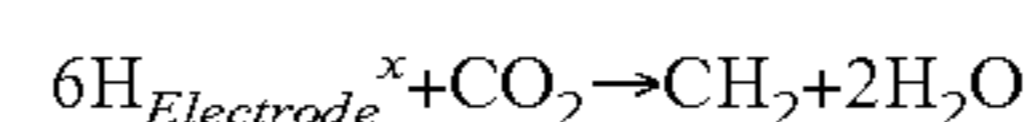
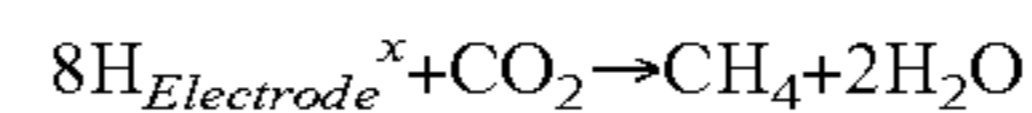
[0078] We add that the total pressure imposed in a cathode or anode compartment may be compensated for in the other compartment so as to have a pressure difference between the two compartments to prevent rupture of the membrane, electrode support assembly if its rupture resistance is too low.

[0079] Concerning the operating temperature T1 of the device, the latter depends on the type of material utilized for membrane 31; in any case, this temperature is over 200° C. and is generally under 800° C., or even under 600° C. This operating temperature corresponds to a conduction ensured by W protons.

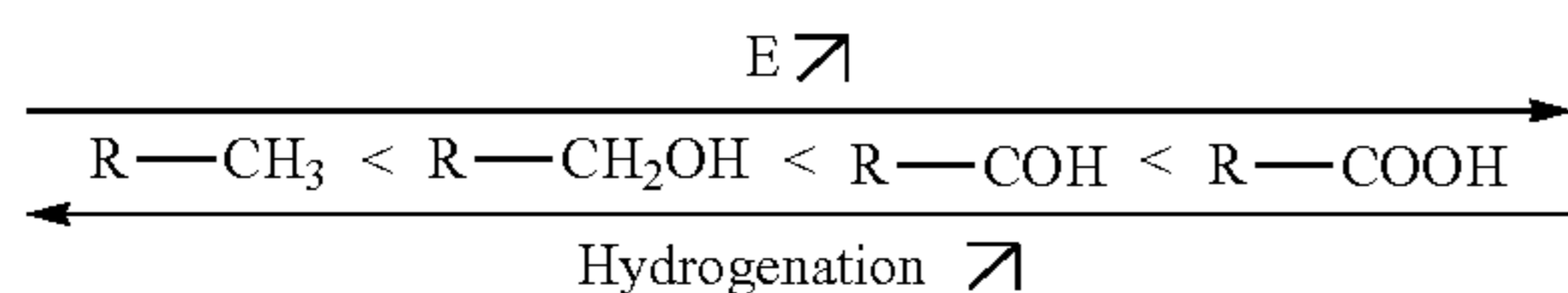
[0080] The operating temperature T1 of the device is also dependent, within the 200 to 800° C. range, according to the nature of the C_xH_yO_z carbon compounds that one wishes to generate.

[0081] In fact, a large variety of compounds may be obtained, such as methane, methanol, formaldehyde, carboxylic acids (formic acid, etc.) and other compounds with longer chains, which may go as far as the formation of synthetic fuel.

[0082] For example, one may have the following reactions at the cathode:



[0083] Concerning the voltage-current pair applied to the cathode, it should be noted that the nature of the carbon compounds formed also depends on this voltage. In fact, the more reductive the cathode medium (low oxidoreduction potential E), the more the carbon compounds generated are hydrogenated, as diagrammed in the diagram below (R being, for example, an alkyl group).



[0084] For the advantageous embodiment of these reactions, it is necessary to have electrodes presenting a large number of triple contact points, i.e., points or contact surfaces between an ionic conductor, an electronic conductor and a gas phase.

[0085] For example, the electrodes considered are preferentially ceramic-metal materials formed by a mixture of ion-conducting ceramic and an electron-conducting metal.

[0086] However, the utilization of “all-ceramic” electron-conducting electrodes may also be considered instead of a ceramic-metal material.

[0087] It should be noted that a given electrolyte may be an O^{2-} proton or ion conductor according to the temperature and the pressure of the applied steam.

[0088] But the utilization of proton-conducting membranes generates hydrogen (in hydrogen atom form more or less adsorbed at the surface of the cathode) that is much more reactive than H_2 hydrogen (or dihydrogen), thus enabling better hydrogenation of the CO_2 and CO compared to a conventional hydrogenation process (in the presence of H_2).

[0089] Moreover, the utilization of H^+ ion conducting membranes operating at moderate temperature enables the synthesis of $\text{C}_x\text{H}_y\text{O}_z$ type complex compounds (with x, y and z greater than 1) while the utilization of O^{2-} conducting membranes, operating at a much higher temperature, preferentially generates CO, a product that is stable at high temperature.

[0090] The objective of studies implemented is to obtain the maximum yield for the production of hydrogen and/or the hydrogenation of CO_2 and/or CO. To do this, most of the current utilized must intervene in the faraday process, i.e., be utilized for the reduction of water and consequently the production of highly reactive hydrogen.

[0091] Thus the voltage utilized for polarization must be affected at least by

[0092] overvoltage at the electrodes

[0093] contact resistance at the electrode/electrolyte interfaces

[0094] ohmic drop within materials and particularly within the electrolyte

[0095] the standard thermodynamic reaction voltage at the electrodes.

[0096] In this context, the present invention proposes the utilization of proton-conducting electrolyte under steam pressure for the electrolysis of water at high temperature for hydrogen production as well as for electroreduction of CO_2 and/or CO at the cathode.

[0097] Thus, the process comprises the following steps:

[0098] the insertion of protonated species under the effect of the pressure of a gas stream containing steam, into said membrane,

[0099] electrolysis of the steam and reduction of the gas (CO_2 and/or CO) in the cathode compartment.

[0100] Thanks to the gas stream containing steam, protonation of the membrane is promoted by the steam under pressure and this pressure is advantageously utilized to obtain the desired conductivity at a given temperature. Such a pro-

cess is described, for example, in the French patent application filed under No. 07/55418 on Jun. 1, 2007.

[0101] As indicated in this application, the applicant observed that the increase in the relative partial pressure of steam leads to an increase in the ionic conductivity of the membrane.

[0102] This correlation between the increase in relative partial pressure with the increase in conductivity enables suitable materials to be worked at lower temperatures. In other words, the lowering in conductivity driven by operating at lower temperatures is compensated for by the increase in relative partial pressure of steam.

[0103] In conformance with the invention, “highly reactive” hydrogen is produced at the cathode that may generate hydrogen (H_2), in the absence of a reducible compound, or $\text{C}_x\text{H}_y\text{O}_z$ type compounds, in the presence of CO_2 and/or CO with $x > 1$; y is between 0 and $2x+2$ and z is between 0 and $2x$.

[0104] The proton-conducting membrane is made from a material promoting the insertion of water such as a doped perovskite material of general formula $\text{AB}_{1-x}\text{D}_2\text{O}_{3-x/2}$. The materials utilized for the anode and the cathode are preferentially ceramic-metal materials (mixture of metal with the perovskite material utilized for the electrolyte). The membrane is preferably impermeable to O_2 and H_2 gases.

[0105] In general, the membrane may be of the type: perovskite vacancies, non-stoichiometric perovskites and/or perovskites doped with general formula ABO_3 , of fluorite, pyrochlore $\text{A}_2\text{B}_2\text{X}_7$, apatite $\text{Me}_{10}(\text{XO}_4)_6\text{Y}_2$, oxyapatite $\text{Me}_{10}(\text{XO}_4)_6\text{O}_2$ structure, of hydroxylapatite $\text{Me}_{10}(\text{XO}_4)_6(\text{OH})_2$ structure, silicate structures, aluminosilicates (phyllosilicate or zeolite), silicates grafted with oxyacids or silicates grafted with phosphates.

[0106] More generally, the electrolytes may advantageously be all of the compounds utilized as high temperature or intermediate temperature proton conductors either by virtue of their tunnel or sheet structure and/or by the presence of vacancies capable of inserting protonated species whose molecular size is small.

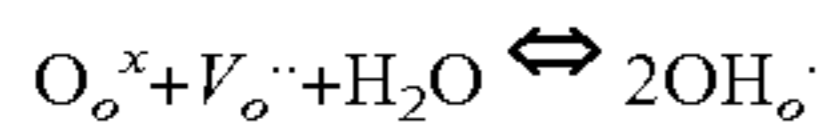
[0107] The present invention is capable of many variations. In particular, the material enabling the incorporation of protonated species may be impermeable to O_2 and H_2 gases and/or may enable the incorporation of protonated species at a densification level of over 88%, preferably equal at least to 94%.

[0108] In fact, a good compromise between the densification level that must be the highest possible (particularly for the mechanical strength of electrolytes and gas permeation) and the capacity of the material to enable incorporation of protonated species must be found. Increasing the partial steam pressure that forces the incorporation of protonated species into the membrane compensates for the densification level increase.

[0109] According to a variation, the material enabling the injection of water is an oxygen atom-defective oxide such as an oxygen-defective perovskite acting as a proton conductor. In addition, the oxygen atom-defective oxide may present stoichiometric intervals and/or may be doped.

[0110] In fact, non-stoichiometry and/or doping allow the creation of oxygen atom vacancies. Thus, in the case of proton conduction, the exposure under pressure of a perovskite presenting stoichiometric intervals and/or being doped (and therefore being deficient in oxygen) to steam induces the incorporation of protonated species into the structure. The

molecules of water fill the oxygen vacancies and dissociate into 2 hydroxyl groups (or H+ proton on an oxide site) according to the reaction:



[0111] It will be noted that materials other than non-stoichiometric and/or doped perovskites may be utilized as materials promoting the incorporation of water and its dissociation in the form of protonated species and/or hydroxides.

[0112] For example, crystallographic structures, such as fluorite structures, pyrochlore $\text{A}_2\text{B}_2\text{X}_7$ structures, apatite $\text{Me}_{10}(\text{XO}_4)_6\text{Y}_2$ structures, oxyapatite $\text{Me}_{10}(\text{XO}_4)_6\text{O}_2$ structures, hydroxylapatite $\text{Me}_{10}(\text{XO}_4)_6(\text{OH})_2$ structures, silicates, aluminosilicates, phyllosilicates, or phosphates may be cited.

[0113] These structures may possibly be grafted by oxyacid groups.

[0114] In fact, all structures having a high affinity with water and/or protons may be contemplated.

1. A process for electrolyzing steam injected under pressure into an anode compartment of an electrolyzer provided with a proton-conducting membrane made of a material enabling protonated species to be incorporated into this membrane under steam, oxidation of the water injected in steam form taking place at the anode so as to generate protonated species in the membrane that migrate within this same membrane and are reduced at the surface of the cathode in the form of reactive hydrogen atoms capable of reducing carbon dioxide CO_2 and/or carbon monoxide CO , said process comprising the following steps:

the introduction of CO_2 and/or CO under pressure into the cathode compartment of the electrolyzer,

the reduction of CO_2 and/or CO introduced into the cathode compartment from said reactive hydrogen atoms generated such that the CO_2 and/or CO form $\text{C}_x\text{H}_y\text{O}_z$ type compounds, with $x \geq 1$; y is between 0 and $2x+2$ and z is between 0 and $2x$.

2. The electrolysis process according to claim 1, wherein the process comprises a step of controlling the nature of the $\text{C}_x\text{H}_y\text{O}_z$ type compounds formed according to the voltage-current pair applied to the cathode.

3. The electrolysis process according to claim 1 wherein the process comprises a step of the utilization of a proton-conducting membrane that is impermeable to the diffusion of oxygen O_2 and H_2 and enables the incorporation of protonated species into this membrane under steam pressure.

4. The electrolysis process according to claim 3, wherein the process comprises a step of utilizing a proton-conducting membrane of the type: perovskite vacancies, non-stoichiometric perovskites and/or perovskites doped with general formula ABO_3 , of fluorite, pyrochlore $\text{A}_2\text{B}_2\text{X}_7$, apatite $\text{Me}_{10}(\text{XO}_4)_6\text{Y}_2$, oxyapatite $\text{Me}_{10}(\text{XO}_4)_6\text{O}_2$ structure, of hydroxylapatite $\text{Me}_{10}(\text{XO}_4)_6(\text{OH})_2$ structure, of silicate structure, aluminosilicates, phyllosilicates, zeolite, silicates grafted with oxyacids or silicates grafted with phosphates.

5. The electrolysis process according to claim 4, wherein the process comprises a step of utilizing, as a proton-conducting membrane, an electrolyte supported by the cathode or by the anode so as to reduce its thickness in order to increase its mechanical strength.

6. The electrolysis process according to claim 1, wherein the process comprises a step of the utilization of a relative partial pressure of steam greater than or equal to 1 bar and less than or equal to a burst pressure of the assembly, the latter being greater than or equal to at least 100 bars.

7. The electrolysis process according to claim 1, wherein the relative partial pressure of steam is advantageously greater than or equal to 50 bars.

8. The electrolysis process according to claim 1, wherein the relative pressure of CO_2 and/or CO is greater than or equal to 1 bar and less than or equal to the burst pressure of the assembly, the latter being greater than or equal to at least 100 bars.

9. The electrolysis process according to claim 1, wherein the electrolysis temperature is greater than or equal to 200°C . and less than or equal to 800°C ., advantageously between 350°C . and 650°C .

10. The electrolysis process according to claim 1, wherein the electrodes, of porous structure, are either ceramic-metal materials, or "ceramic" electrodes with mixed electronic and ionic conduction.

11. The electrolysis process according to claim 10, wherein the ceramic-metal materials are, for the cathode, ceramic-metal materials in which the ceramic is compatible with the electrolyte forming the membrane and in which the nature of the metal dispersed is advantageously a metal and/or a metal alloy among which metals such as cobalt, copper, molybdenum, silver, iron, zinc, noble metals (gold, platinum, palladium) and/or transition elements may be cited.

12. The electrolysis process according to claim 10, wherein the ceramic-metal materials are, for the anode, ceramic-metal materials in which the ceramics are compatible with the electrolyte forming the membrane and in which the nature of the metal dispersed is advantageously a metal alloy or a passivable metal.

13. A steam electrolysis device for electrolyzing steam introduced under pressure into an anode compartment of an electrolyzer provided with a proton-conducting membrane, made of a material enabling the injection of protonated species into this membrane under steam after oxidation, comprising:

an electrolyte in the form of an ion conducting membrane made in said material enabling the injection of protonated species under the effect of the water pressure in said membrane,

an anode,

a cathode,

a generator enabling current to be generated and to apply a potential difference between said anode and said cathode,

means for the insertion of steam under pressure in said electrolyte via said anode,

means to inject CO_2 and/or CO under pressure into the cathode compartment of the electrolyzer, and

means to reduce the CO_2 and/or the CO introduced into the cathode compartment according to a process in conformance with one of the previous embodiments.

14. The device according to claim 13, wherein the material enabling the injection of protonated species is impermeable to O_2 and H_2 gases.

15. The device according to claim 13, wherein the material enabling the injection of protonated species has a densification level of over 88%, preferably equal at least to 94%.

16. The device according to claim 13, wherein the material enabling the injection of protonated species is an oxygen atom-defective oxide such as an oxygen-defective perovskite acting as a proton conductor.

17. The device according to claim 16, wherein the oxygen atom-defective oxide presents stoichiometric intervals and/or is doped.