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Sala et al.(10) **Pub. No.: US 2014/0284220 A1**(43) **Pub. Date: Sep. 25, 2014**(54) **METHOD FOR GENERATING HYDROGEN
AND OXYGEN BY STEAM ELECTROLYSIS****Publication Classification**(71) Applicant: **AREVA**, Paris (FR)(51) **Int. Cl.**
C25B 1/04 (2006.01)(72) Inventors: **Béatrice Sala**, Saint Gely Du Fesc (FR);
Frédéric Grasset, Montpellier (FR);
Olivier Lacroix, Montpellier (FR);
Abdelkader Sirat, Montpellier (FR);
Kamal Rahmouni, Montpellier (FR);
Michel Keddou, Paris (FR); **Hisasi
Takenouti**, Ollainville (FR); **Dominique
Goeuriot**, Monistrol Sur Loire (FR);
Baroudi Bendjeriou, Saint-Etienne
(FR); **Philippe Colombar**, Fresnes (FR);
Arie Van Der Lee, Castelnau-Le-Lez
(FR); **José Grégorio Sanchez**,
Sussargues (FR)(52) **U.S. Cl.**
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USPC **205/629; 204/275.1**(57) **ABSTRACT**

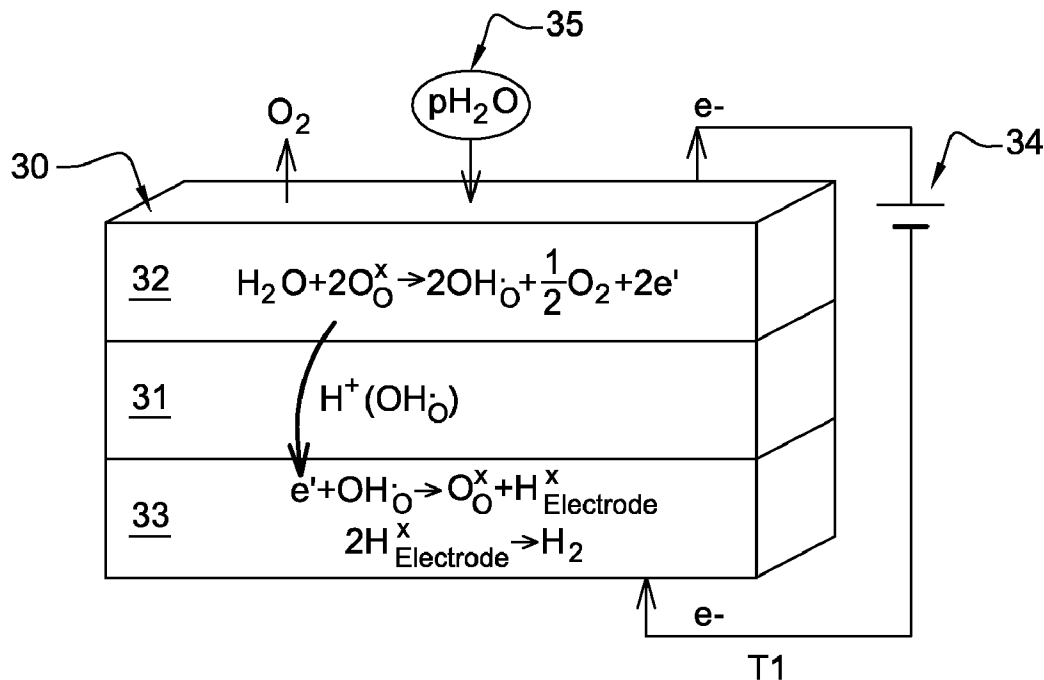
The present invention relates to a method for generating hydrogen and oxygen adsorbates by steam electrolysis at 200 to 800° C. using an electrolysis cell (30) comprising a solid electrolyte (31) which is made of a proton-conducting ceramic and which is arranged between an anode (32) and a cathode (33), each of which comprises a proton-conducting ceramic, and the ratio of the electroactive surface to the geometric surface of each of which is equal to at least 10, said method comprising the following steps: circulating a current between the anode (32) and the cathode (33), wherein the density of the current is no less than 500 mA/cm²; inserting water in the form of steam, which is fed under pressure to the anode (32); oxidizing said water in the form of steam at the anode (32), and generating highly reactive oxygen at the anode (32) after said oxidation; generating protonated species in the electrolyte (31) after said oxidation and migrating said protonated species in the electrolyte (31); and reducing said protonated species at the surface of the cathode (33) in the form of reactive hydrogen atoms.

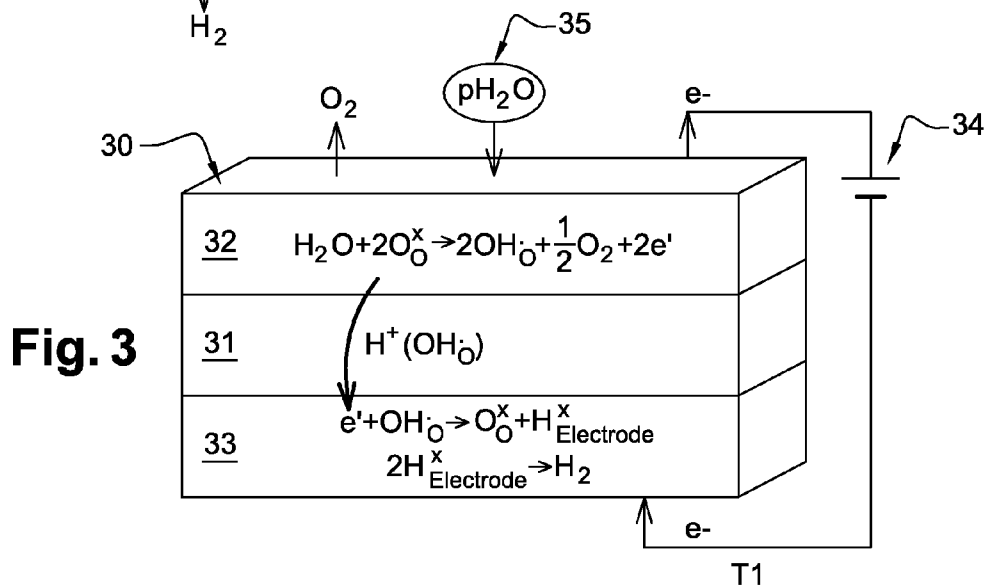
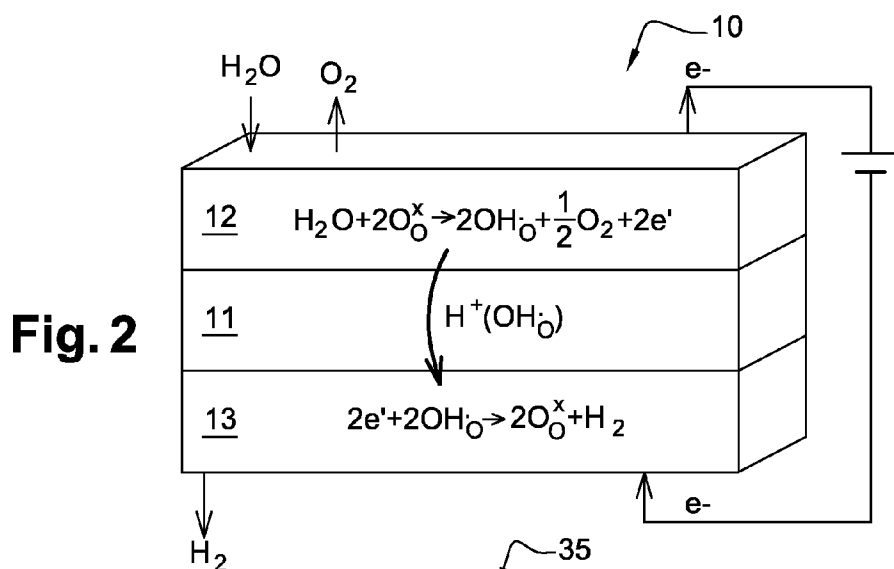
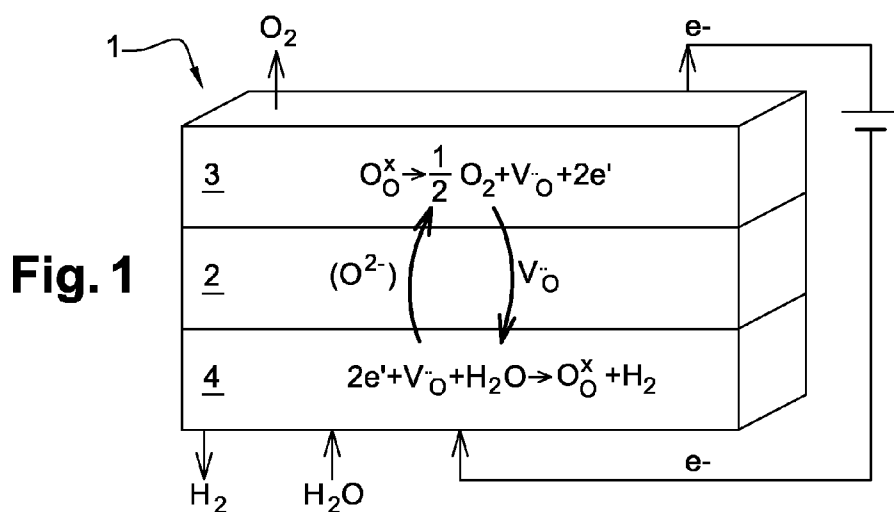
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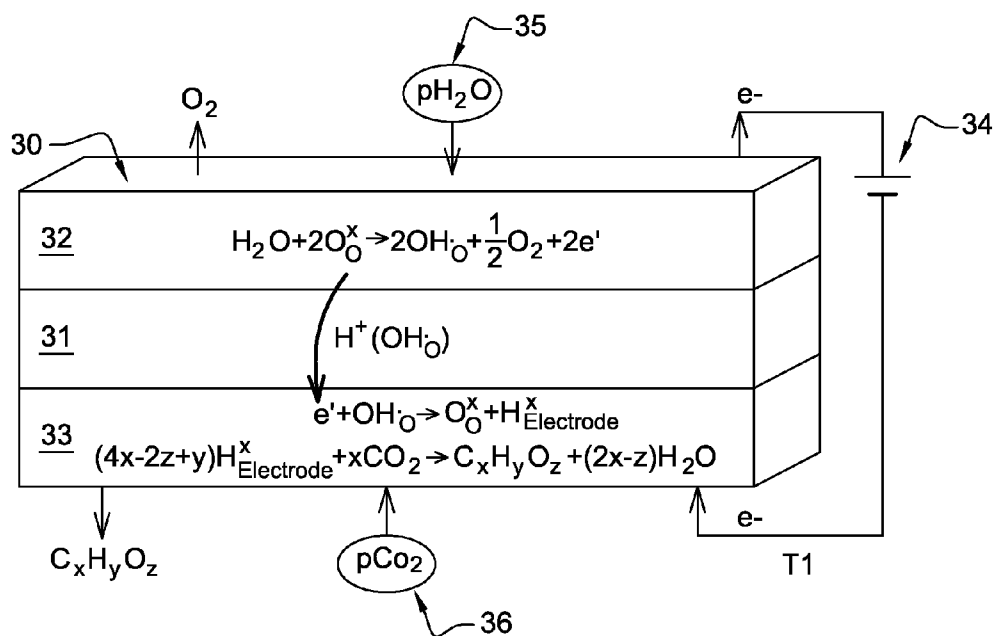


Fig. 4

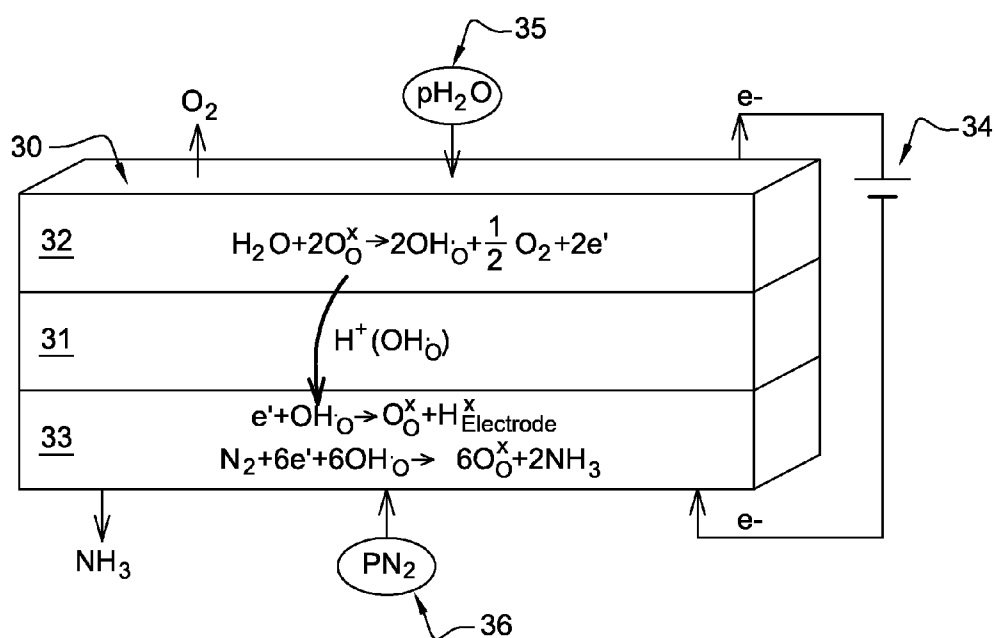


Fig. 6

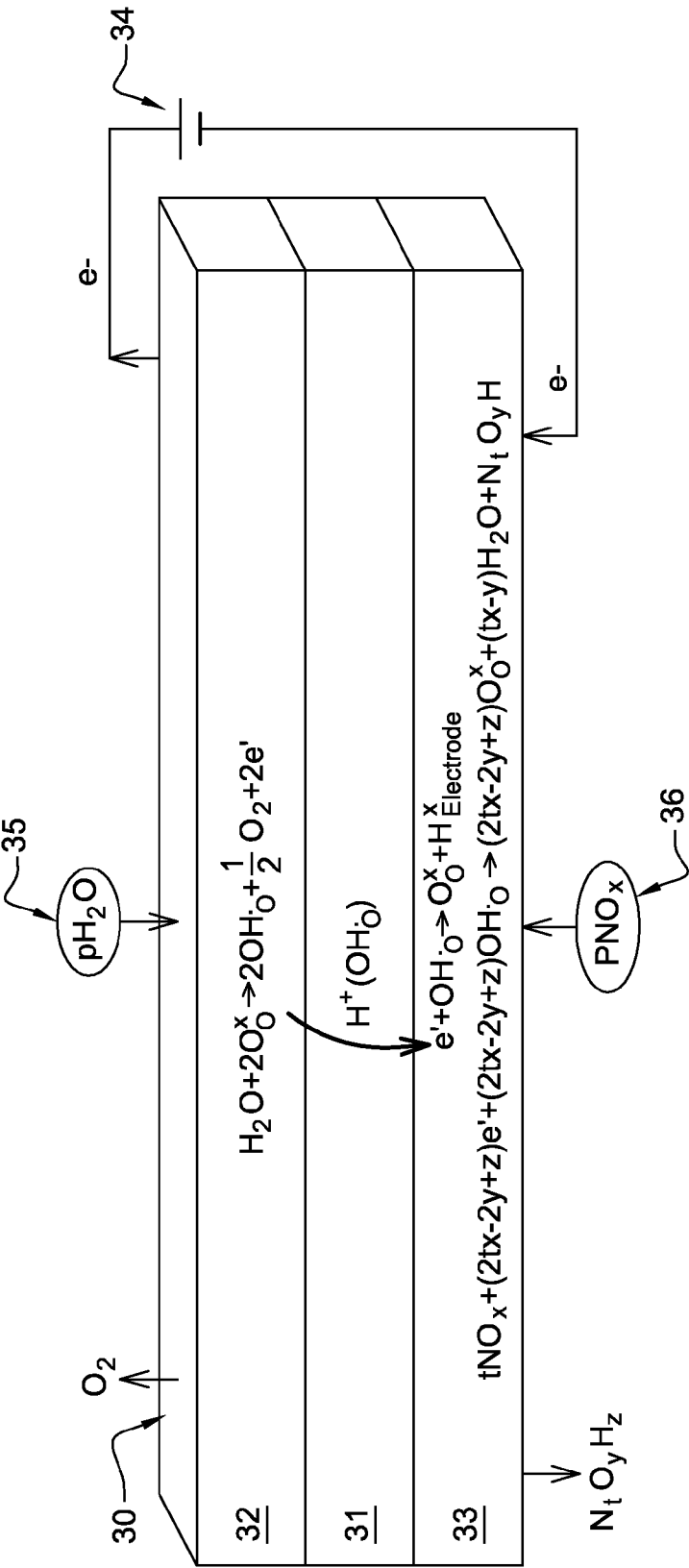


Fig. 5

METHOD FOR GENERATING HYDROGEN AND OXYGEN BY STEAM ELECTROLYSIS

[0001] The present invention relates to a method for generating highly reactive hydrogen and oxygen by steam electrolysis by means of a proton-conducting membrane.

[0002] Conductive ceramic membranes are today the subject of widespread research to increase their performances; in particular, said membranes find particularly interesting applications in fields such as the electrolysis of water at high temperature for the production of hydrogen or the treatment of carbon gases (CO₂, CO) by electrochemical hydrogenation. Patent applications WO2008152317 and WO2009150352 describe examples of such methods.

[0003] Hydrogen (H₂) appears today as a very interesting energy vector, which is likely to take more and more importance for treating among others petroleum products, and which could, in the longer term, advantageously act as a substitute for oil and fossil fuels, the reserves of which are going to decrease considerably over coming decades. In this perspective, it is nevertheless necessary to develop efficient methods of producing hydrogen.

[0004] Numerous methods for producing hydrogen, from different sources, have certainly been described but many of said methods prove to be unsuitable for massive industrial production of hydrogen.

[0005] In this context, the synthesis of hydrogen from the steam reforming of hydrocarbons may be cited for example. One of the major problems of this synthesis route is that it generates, as sub-products, important quantities of greenhouse gases of CO₂ type. In fact, 8 to 10 tonnes of CO₂ are released to produce 1 tonne of hydrogen.

[0006] Two challenges thus arise for future years: searching for a novel energy vector that can be used without danger for our environment, such as hydrogen, and reducing the quantity of carbon dioxide.

[0007] Technical-economic estimations of industrial methods now take this latter piece of information into account. However, it mainly involves sequestration, in particular underground sequestration in anfractuosités that do not necessarily correspond to former oil reservoirs, which in the long run may not be without danger.

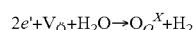
[0008] A promising way forward for the industrial production of hydrogen is the technique known as steam electrolysis, for example at high temperature (HTE), at moderate temperature, typically above 200° C., or instead at intermediate temperature comprised between 200° C. and 1000° C.

[0009] At the present time, two steam electrolysis production methods are known:

[0010] According to a first method illustrated in FIG. 1, an electrolyte is used that is capable of conducting O²⁻ ions and operating at temperatures generally comprised between 750° C. and 1000° C.

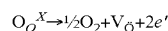
[0011] More specifically, FIG. 1 schematically represents an electrolyser 1 comprising a ceramic membrane 2, conducting O²⁻ ions, assuring the function of electrolyte separating an anode 3 and a cathode 4.

[0012] The application of a potential difference between the anode 3 and the cathode 4 leads to a reduction of the steam H₂O on the side of the cathode 4. This reduction forms hydrogen H₂ and O²⁻ ions (O_O^X in the Kröger-Vink notation) at the surface of the cathode 4 according to the reaction:



[0013] The O²⁻ ions, more specifically the oxygen vacancies (V_O), migrate through the electrolyte 2 to form oxygen

O₂ at the surface of the anode 3, electrons e⁻ being released according to the oxidation reaction:

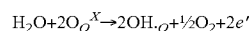


[0014] Thus, this first method makes it possible to generate at the outlet of the electrolyser 1 oxygen—anodic compartment—and hydrogen mixed with steam—cathodic compartment.

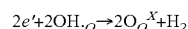
[0015] According to a second method illustrated in FIG. 2, an electrolyte is used that is capable of conducting protons and operating at lower temperatures than those required by the first method described above, generally comprised between 200° C. and 800° C.

[0016] More specifically, this FIG. 2 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.

[0017] The application of a potential difference between the anode 12 and the cathode 13 causes an oxidation of the steam H₂O on the side of the anode 12. The steam fed into the anode 12 is thus oxidised to form oxygen O₂ and H⁺ ions (or OH_O in the Kröger-Vink notation), this reaction releasing electrons e⁻ according to the equation:



[0018] The H⁺ ions (or OH_O in the Kröger-Vink notation) migrate through the electrolyte 11, to form hydrogen H₂ at the surface of the cathode 13 according to the equation:



[0019] Thus, this method provides at the outlet of the electrolyser 10 pure hydrogen—cathodic compartment—and oxygen mixed with steam—anodic compartment.

[0020] More specifically, the formation of H₂ goes through the formation of intermediate compounds, which are atoms of hydrogen 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 the Kröger-Vink notation). These species being highly reactive, they usually recombine to form hydrogen H₂ according to the equation:



[0021] The patent application WO2008152317 has shown that the insertion of steam under pressure makes it possible to remain at moderate operating temperatures (of the order of 500 to 600° C.) while obtaining conductivity values assured by the movement of relatively high H⁺ protons.

[0022] Nevertheless, this type of proton-conducting electrolysis is above all studied and developed at the laboratory level with low current levels. Some fear, as in the case of O²⁻ conducting electrolysis, phenomena of delamination of the electrode, which can induce decohesion between said electrode and the electrolyte during use with higher current densities.

[0023] In fact, unlike the field of anionic-conducting electrolyses, the charge carriers (protons) are not intrinsic to the structure of the membrane and are thus consequently more limited in the structure than the charge carriers of an anionic conduction, which are formed by the vacancies of the structure.

[0024] Consequently, it is known to use in the field of anionic-conducting electrolyses current densities at the terminals of the electrodes greater than the current densities used in the field of proton-conducting electrolyses.

[0025] Nevertheless, the application of such current densities at the terminals of the electrodes of a proton-conducting electrolyser in electrolysers of the prior art would cause localised over-voltages which would lead to phenomena of delamination of the electrodes.

[0026] In this context, the present invention aims to propose a method for generating highly reactive hydrogen and oxygen adsorbates by steam electrolysis using an electrolysis cell comprising a solid proton-conducting electrolyte, said method being able to be industrialised while limiting the risks of delamination of the electrodes.

[0027] To this end, the invention proposes a method for generating hydrogen and oxygen adsorbates by steam electrolysis at 200° C. to 800° C. using an electrolysis cell comprising a solid electrolyte, which is made of a proton-conducting ceramic, said electrolyte being arranged between an anode and a cathode, said anode and cathode each comprising a proton-conducting ceramic and the ratio of the electroactive surface to the geometric surface of each of which is equal to at least 10, said method comprising the following steps:

[0028] circulating a current between the anode and the cathode, wherein the density of the current is no less than 500 mA/cm²;

[0029] inserting water in the form of steam, which is fed under pressure to the anode;

[0030] oxidizing said water in the form of steam at the anode;

[0031] generating highly reactive oxygen at the anode after said oxidation;

[0032] generating protonated species in the electrolyte after said oxidation;

[0033] migrating said protonated species in the electrolyte;

[0034] reducing said protonated species at the surface of the cathode in the form of reactive hydrogen atoms.

[0035] It will be noted that the current may be continuous or pulsed; in the case of a pulsed current, current density is taken to mean the current density corresponding to the maximum value of the current intensity reached during the pulse.

[0036] The generation of the current may be obtained by different means:

[0037] a generator imposing a voltage at the terminals of the assembly (i.e. a potential difference between the electrodes) may be used;

[0038] a current source imposing a current between the electrodes may be used;

[0039] operation in potentiostatic mode may also be used; in other words, in addition to the two cathode and anode electrodes, at least one third electrode known as reference is used. The working electrode (preferentially the cathode) is then going to be taken to a given potential with respect to the reference electrode (in which one avoids passing too much current so as not to modify its potential that serves as reference). The generator making it possible to maintain automatically the potential of the working electrode, even under current, is known as a potentiostat.

[0040] As explained above, reactive hydrogen atoms are taken to mean hydrogen atoms adsorbed at the surface of the cathode and/or radical hydrogen atoms H. (or H_{Electrode}^X in the Kröger-Vink notation).

[0041] Geometric surface of an electrode is taken to mean its flat external surface and electroactive surface is taken to mean the surface constituted of the internal surface of the

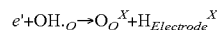
pores of the electrode wherein takes place the electrochemical reaction; in other words, it is the internal surface on which the reaction takes place: $2e^- + 2OH_{O^-} \rightarrow 2O_{O^-}^X + H_2$. The electrodes according to the invention thus have a large number of triple points, namely points or contact surfaces between an ionic conductor, an electron conductor and a gas phase.

[0042] The invention results from the finding made by the applicant that the use of electrodes (cathode and anode) comprising a proton-conducting ceramic (typically electrodes formed of a cermet including a mixture of said ceramic of perovskite type and a metal alloy and/or a perovskite doped with a lanthanide with one or more degrees of oxidation) surrounding a proton-conducting electrolyte and having a sufficiently high electroactive surface/geometric surface ratio makes it possible to work at much higher current densities than those provided in the prior art without risk of delamination of said electrodes.

[0043] In fact, the consequent increase of the ratio between the electroactive surface and the geometric surface of the electrodes compared to the ratio of electrodes of the prior art makes it possible to reduce local over-voltages, which are responsible for phenomena of delamination of the electrodes.

[0044] The method according to the invention generates highly reactive hydrogen at the cathode of the electrolyser (particularly hydrogen atoms adsorbed on the surface of the electrode and/or radical hydrogen atoms).

[0045] These highly reactive hydrogen atoms H_{Electrode}^X are formed at the surface of the cathode according to the reaction:



[0046] These highly reactive hydrogen atoms may be used as such for the production of hydrogen or for other applications that will be detailed hereafter.

[0047] 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:

[0048] in a particularly advantageous manner, said ratio between the electroactive surface and the geometric surface of said cathode and anode is no less than 100; such a ratio makes it possible to further improve the resistance of the electrodes at high current densities without risk of delamination;

[0049] said density of the current is no less than 1 A/cm²;

[0050] the partial and relative steam pressure is advantageously no less than 1 bar and preferentially no less than 10 bars;

[0051] the circulation of the current takes place between an anode and a cathode, each made of a cermet constituted of a mixture of a proton-conducting ceramic and a conducting material;

[0052] said conducting material is a passivable material with high melting point being able to comprise at least 40% of chromium;

[0053] the circulation of the current takes place between an anode and a cathode, each comprising a proton-conducting ceramic formed of a perovskite doped with a lanthanide with one or more degrees of oxidation, said ceramic being doped with a complementary doping element taken from the following group: niobium, tantalum, vanadium, phosphorous, arsenic, antimony, bismuth;

- [0054] the method according to the invention comprises the following steps:
- [0055] introducing carbon dioxide CO_2 and/or carbon monoxide CO at the cathode of the electrolysis cell;
- [0056] reducing the CO_2 and/or CO introduced at the cathode from said generated reactive hydrogen atoms;
- [0057] forming $\text{C}_x\text{H}_y\text{O}_z$ 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 CO ;
- [0058] the method according to the invention comprises the following steps:
- [0059] introducing nitrogen containing compounds at the cathode of the electrolysis cell;
- [0060] reducing said nitrogen containing compounds introduced at the cathode from said generated reactive hydrogen atoms;
- [0061] said nitrogen containing compounds are NO_x type compounds where $x \geq 1$, said method comprising a step of forming $\text{N}_t\text{O}_y\text{H}_z$ type compounds, where t is no less than 1, y no less than 0 and z no less than zero, after the reduction of the NO_x ;
- [0062] said nitrogen containing compounds are N_2 compounds, said method comprising a step of forming N_xH_y type compounds, where $x \geq 1$ and $y \geq 0$, to result in the formation of NH_3 after the reduction of the N_2 ;
- [0063] said reactive hydrogen atoms are used to carry out a step of hydrocracking at the cathode;
- [0064] said reactive hydrogen atoms are used to convert aromatic compounds at the cathode, for example into saturated alkanes (paraffins) or into cycloalkanes (naphthenes);
- [0065] the method according to the invention comprises a step consisting in making said highly reactive oxygen react with a compound introduced at the anode such that the latter undergoes oxygenation.
- [0066] The subject matter of the present invention is also an electrolysis cell for the implementation of the method according to the invention comprising:
- [0067] a solid electrolyte, which is made of a proton-conducting ceramic;
- [0068] an anode comprising a proton-conducting ceramic, said anode and cathode each having a ratio between its electroactive surface and its geometric surface equal to at least 10;
- [0069] a cathode comprising a proton-conducting ceramic, said electrolyte being arranged between said anode and said cathode;
- [0070] means for inserting water in the form of steam, which is fed under pressure to the anode;
- [0071] means for inducing a current circulating between the anode and the cathode, wherein the density of the current is no less than 500 mA/cm^2 .
- [0072] Said means for inducing a current circulating between the anode and the cathode may be a voltage, current generator or a potentiostat (in this case, the cell will also comprise at least one cathodic or anodic reference electrode).
- [0073] Depending on the applications, the cell may also comprise means of introducing and evacuating pressurised gas in the cathodic compartment and/or means of introducing and evacuating pressurised gas in the anodic compartment.
- [0074] Other characteristics and advantages of the invention will become clear from the description that is given thereof below, as an indication and in no way limiting, with reference to the appended figures, among which:
- [0075] FIGS. 1 and 2, already described, are simplified schematic representations of steam electrolyzers,
- [0076] FIG. 3 is a general simplified schematic representation of an electrolysis cell for the implementation of the method according to the invention;
- [0077] FIGS. 4 to 6 are illustrations of applications using the cell of FIG. 3.
- [0078] FIG. 3 represents in a general, schematic and simplified manner an electrolysis cell 30, also known as elementary assembly, implementing the electrolysis method according to the invention.
- [0079] This electrolysis cell 30 has a structure similar to that of the device 20 of FIG. 2. Thus, the cell 30 comprises:
- [0080] an anode 32,
- [0081] a cathode 33,
- [0082] an electrolyte 31 formed of a proton-conducting electrolytic membrane,
- [0083] means 34 for inducing a current circulating between the anode 32 and the cathode 33, wherein the density of the current is no less than 500 mA/cm^2 ,
- [0084] means 35 making it possible to insert under pressure steam pH_2O into the membrane 31 via the anode 32 (the partial and relative steam pressure of the current is no less than 1 bar and preferentially no less than 10 bars).
- [0085] It will be noted that the term partial and relative pressure here designates the insertion pressure compared to atmospheric pressure.
- [0086] It will be noted that it is possible to use either a gaseous current containing uniquely steam or a gaseous current containing partially steam. Thus, depending on the case, the term "partial pressure" will designate either the total pressure of the gaseous current in the case where the latter is uniquely constituted of steam or the partial pressure of steam in the case where the gaseous current comprises gases other than steam.
- [0087] According to a first embodiment, the anode 32 and the cathode 33 are preferentially formed of a cermet constituted of a mixture of a proton-conducting ceramic and an electron-conducting passivable alloy that is able to form a passive protection layer so as to protect it in an oxidising environment (i.e. at the anode of an electrolyser). This passivable alloy is preferentially a metal alloy.
- [0088] The passivable alloy comprises for example chromium (and preferentially at least 40% of chromium) so as to have a cermet having the particularity of not oxidising at temperature. The chromium content of the alloy is determined so 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.
- [0089] 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.
- [0090] The ceramic of the anodic and cathodic electrodes 32 and 33 is advantageously the same ceramic as that used by the formation of the electrolytic membrane of the electrolyte 31.
- [0091] According to an advantageous embodiment of the invention, the proton-conducting ceramic used by the forma-

tion of the cermet of the electrodes **32** and **33** and of 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.

[0092] 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 specifically 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** must have a porosity level below 6% (or a density above 94%).

[0093] Advantageously, the sintering of the ceramic is carried out under a reducing atmosphere so as to avoid oxidation of the metal at high temperature, i.e. under atmosphere of hydrogen (H_2) and argon (Ar), or even carbon monoxide (CO) if there is no risk of carburization.

[0094] The electrodes **32** and **33** of the cell **30** are also sintered at a temperature above $1500^\circ C$. (according to the example of sintering of a zirconate type ceramic).

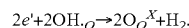
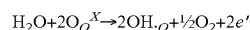
[0095] According to a second embodiment, the anode **32** and the cathode **33** may also be formed of a ceramic material that is a perovskite doped with a lanthanide. The perovskite may be a zirconate of formula $AZrO_3$. The zirconate is doped with a lanthanide that is for example erbium. Moreover, the perovskite doped with a 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 pass 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 electron-conducting. The ceramic is then a ceramic with mixed conduction; in other words, it is conducting both to electrons and to protons whereas in the absence of these 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 both of protons and electrons, and does so even when the ceramic is not mixed with a metal (as is the case of the first embodiment).

[0096] According to the invention, the electrodes **32** and **33** of the cell **30** are designed to have a ratio of their electroactive surface to their geometric surface that is equal to at least 10 and preferentially no less than 100.

[0097] Geometric surface is taken to mean the flat external surface of the electrode, i.e. the surface receiving the flux of electrons.

[0098] Specific (or developed) surface is taken to mean the surface accessible to a gas within the electrode: it is thus essentially constituted of the internal surface of the pores.

[0099] Electroactive surface is taken to mean the part of the specific surface on which the electrochemical reaction takes place; in other words, it is the internal surface on which the reaction takes place:



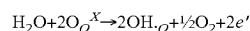
[0100] According to the invention, the means **34** making it possible to inject a current circulating between the anode **32** and the cathode **33**, wherein the density of the current is no less than 500 mA/cm^2 and preferentially no less than 2 A/cm^2 without risk of drop of current or delamination of the electrodes.

[0101] The applicant has advantageously noted that the fact of using electrodes made of a proton-conducting material and having a sufficient electroactive surface (advantageously no less than 100) makes it possible to increase notably the current density that can be used without risk of delamination of the electrodes.

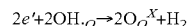
[0102] The determination of the ratio between the electroactive surface and the geometric surface is carried out for example by means of a method of characterising the porous surface of a cermet electrode detailed in the publication "Characterization of porous texture of cermet electrode for steam electrolysis at intermediate temperature", C. Deslouis, M. Keddad, K. Rahmouni, H. Takenouti, F. Grasset, O. Lacroix, B. Sala, *Electrochimica Acta* 56 (2011) 7890-7898.

[0103] The general operation of the cell is described below.

[0104] The circulation of the current between the anode **32** and the cathode **33** causes an oxidation of steam H_2O on the side of the anode **32**. The steam fed under pressure into the anode **32** is thus oxidised to form oxygen O_2 and H^+ ions (or $OH_{\cdot O}$ in the Kröger-Vink notation), this reaction releasing electrons e^- according to the equation:



[0105] The H^+ ions (or $OH_{\cdot O}$ in the Kröger-Vink notation) migrate through the electrolyte **31**, to form hydrogen H_2 at the surface of the cathode **33** according to the equation:



[0106] Thus, this method provides at the outlet of the cell **30** pure hydrogen—cathodic compartment—and oxygen mixed with steam—anodic compartment.

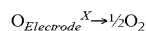
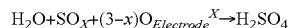
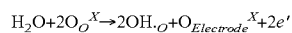
[0107] More specifically, the formation of H_2 goes through the formation of intermediate compounds, which are hydrogen atoms adsorbed at the surface of the cathode **33** and/or radical hydrogen atoms H. (or $H_{\text{Electrode}}^X$ in the Kröger-Vink notation). These species being highly reactive,

[0108] either they recombine to form hydrogen H_2 according to the equation: $2H_{\text{Electrode}}^X \rightarrow H_2$ (cf. FIG. 3);

[0109] or they react with other compounds injected on the cathodic side **33** (as will be seen with reference to FIG. 4 and following figures).

[0110] It will be noted that the oxygen atoms adsorbed at the surface of the anode **32** may advantageously be used to carry out the production of oxygen adsorbate $O_{\text{Electrode}}^X$ being able to be used in an oxygenation reaction at the anode, for example by injecting sulphur dioxide SO_2 or SO_X at the anode, which reacts with oxygen to form sulphuric acid

H₂SO₄ or to form oxygen for the oxycombustion. One thus has for example the following equations:



[0111] Concerning the operating temperature T1 of the device 30, the latter depends on the type of material used for the membrane 31; whatever the case, said temperature is above 200° C. and generally below 800° C., or even below 600° C. Said operating temperature corresponds to a conduction assured by H⁺ protons.

[0112] FIG. 4 and following each illustrate a particular use of the cell 30 of FIG. 3, in which highly reactive hydrogen is used to recombine with other compounds at the cathode 33.

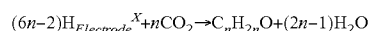
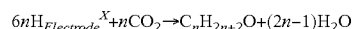
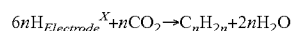
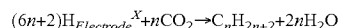
[0113] FIG. 4 illustrates a first example in which the electrolysis cell 30 is used to form compounds of C_xH_yO_z type, (where x≥1, 0<y≤(2x+2) and 0≤z≤2x) after the reduction of the CO₂ and/or CO.

[0114] The cell 30 of FIG. 3 further comprises means 36 making it possible to insert under pressure gas (pCO₂ or/and CO) in the cathodic compartment 33.

[0115] At the anode 32, the water is oxidised while releasing electrons while H⁺ ions (in OH_O form) are generated.

[0116] These H⁺ ions migrate through the electrolyte 31 and are thus capable of reacting with different compounds, which could be injected at the cathode 33, CO₂ and/or CO type carbon compounds reacting at the cathode 33 with said H⁺ ions to form C_xH_yO_z type compounds (where x≥1, 0<y≤(2x+2) and 0≤z≤2x) and water at the cathode.

[0117] The chemical equations of the different reactions may in particular be written:



[0118] 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:



[0119] The nature of the C_xH_yO_z compounds synthesised at the cathode 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 potential/current couple applied at the cathode, the dwell time of the gas and the nature of the electrodes.

[0120] Concerning the pressure of the gases, the relative pressure of CO₂ and/or CO of the current is no less than 1 bar and no more than the rupture pressure of the assembly.

[0121] It should be pointed out that the total pressure imposed in a compartment—cathodic or anodic—may be compensated in the other compartment so as to have a pressure difference between the two compartments to avoid the rupture of the membrane assembly, electrode support if this has a too low rupture strength.

[0122] The operating temperature T1 of the device 30 also depends, in the range between 200 and 800° C., on the nature of the C_xH_yO_z carbon compounds that it is wished to generate.

[0123] FIG. 5 illustrates a second example in which the electrolysis cell 30 is used to reduce NO_x type compounds (x≤2) to form N_tO_yH_z type compounds (where t≥1, y≥0 and z≥0).

[0124] The cell 30 of FIG. 3 further comprises means 36 making it possible to insert under pressure NO_x type compounds (x≤2) into the cathodic compartment 33.

[0125] The problem consists in enabling the reduction by electro-catalytic hydrogenation of the NO_x content of effluents produced for example during the combustion of hydrocarbons or gas. The production of these molecules is 60% due to urban transport and 40% due to boilers and thermal power plants. These molecules easily penetrate the bronchioles and affect respiration, causing hyper reactivity of the bronchial tubes in asthmatics, as well as increased vulnerability of the bronchial tubes to microbes, at least in children. Consequently, the regulations in force require industries to limit their NO_x discharges.

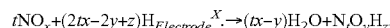
[0126] It is known to those skilled in the art to reduce NO_x by two types of method: selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR). Whatever the solution retained (i.e. with or without catalyst), the latter is based on the use of ammonia to reduce the NO_x into N₂. These solutions have the drawback of using ammonia as hydrogen vector whereas it would be more interesting to directly treat the NO_x with hydrogen. The production of ammonia assumes in fact using a method of steam reforming of hydrocarbons generating CO₂. This method furthermore implies the use of a second reactor for the production of ammonia.

[0127] The method of using the cell 30 according to FIG. 5 is based on the following principle: pressurised steam is introduced at the anodic compartment 32 and the NO_x is fed under pressure at the cathodic compartment 33. The incorporation under pressure of steam is going to lead to oxidation of this water in the form of steam at the surface of the anode so as to generate protonated species in the membrane which, after migration within the membrane, are reduced at the surface of the cathode into very reactive hydrogen capable of reducing by hydrogenation the NO_x introduced into the cathodic compartment, such that the NO_x are reduced into less oxidised NO_y (where y≤x), then into nitrogen then into ammonia.

[0128] Thus, in the solution proposed, in a single reactor (i.e. the cell 30) are combined the generation of protons and the electro-catalytic hydrogenation of NO_x.

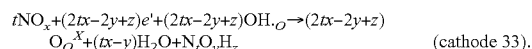
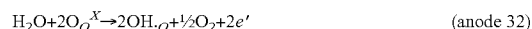
[0129] The monoatomic hydrogen adsorbates are formed at the surface of the cathode 33 according to the reaction: e' + OH_O → O_O^X + H_{Electrode}^X.

[0130] Consequently, in the presence of NO_x on the cathodic side 33, the very reactive adsorbates H_{Electrode}^X react with the nitrogen containing compounds at the cathode 33 to give reduced compounds of nitrogen oxides of N_tO_yH_z type, where x≥1 and y≥0 and z≥0 according to the reaction:



[0131] As an example, these compounds are either NO_y, less oxidised than the NO_x compounds fed in under pressure, nitrogen N₂, or ammonia NH₃.

[0132] The overall reactions at the electrodes are written:



[0133] The solution according to the invention makes it possible to reduce the number of reactors required for the

reduction of NO_x to a single and unique reactor accommodating the electro-hydrogenation.

[0134] FIG. 6 illustrates a third example in which the electrolysis cell 30 is used to produce ammonia by electro-catalytic hydrogenation of N₂. It should be noted that, according to this embodiment, it is also possible to produce other N_xH_y type compounds where x≥1 and y≥0 before resulting in the formation of NH₃.

[0135] The cell 30 of FIG. 3 further comprises means 36 making it possible to insert nitrogen N₂ under pressure into the cathodic compartment 33.

[0136] The problem is here to produce in massive quantity, at low cost and without emission of CO₂, ammonia, by electro-catalytic hydrogenation of N₂.

[0137] At present, ammonia is produced by catalytic hydrogenation reaction of N₂ during steam reforming of hydrocarbons. The synthesis of this product thus indirectly emits CO₂. In addition, the synthesis method induces a very great volatility of the production price of NH₃. In fact 80% of the price of NH₃ is directly dependent on the price of the gas from which is produced the hydrogen required for the synthesis. Thus, the volatility of the price of ammonia is very high and dependent on that of the gas.

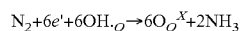
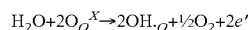
[0138] Moreover, according to known techniques, even when hydrogen is produced by electrolysis, it is necessary to use two reactors, one for the production of hydrogen and the other for the catalytic reaction.

[0139] The solution implemented in the cell 30 of FIG. 6 aims to produce ammonia using a single reactor.

[0140] As previously, the hydrogenated monoatomic compounds are formed at the surface of the cathode according to the reaction: $e' + OH_{\text{O}} \rightarrow O_{\text{O}}^X + H_{\text{Electrode}}^X$.

[0141] Consequently, in the presence of N₂ on the cathodic side 33, very reactive hydrogen H_{Electrode}^X reacts with the hydrogenated compounds on the electrode 33 to give NH₃ according to the reaction: $N_2 + 6H_{\text{Electrode}}^X \rightarrow 2NH_3$.

[0142] The overall reactions at the electrodes are written:



[0143] The solution of FIG. 6 makes it possible to reduce the number of reactors required for the production of NH₃ (which serves as H₂ vector) to a single and unique reactor accommodating the electro-hydrogenation.

[0144] In the solution proposed, the hydrogen required for the reduction of the nitrogen is no longer produced from fossil energy; the method according to the invention is "cleaner" in so far as it does not generate CO₂.

[0145] Moreover, such a method makes it possible to do without the use of catalyst, which it is necessary to change and to recycle on account of its deactivation by the water produced during the catalytic reduction reaction.

[0146] Finally, the solution proposed makes it possible to avoid a storage of H₂ since the reactions of production of reactive hydrogen and reduction by hydrogenation take place in the same reactor.

[0147] As it has been possible to see with reference to FIGS. 4 to 6, the highly reactive hydrogen produced by the cell 30 of FIG. 3 may be used industrially for very different applications. Obviously, the invention is not limited to the embodiments that have been described. Thus, the hydrogenation by the highly reactive hydrogen atoms may also be used in the petrochemical industry, for example to convert aromatic compounds into saturated alkanes (paraffins) and

into cycloalkanes (naphthenes). The method according to the invention may also be used to carry out hydrocracking making it possible to convert, under hydrogen pressure and at sufficiently high temperature, heavy petroleum products into light products: typically, hydrocracking makes it possible to obtain products such as diesel oil or kerosene from heavy residues.

1. Method for generating hydrogen and oxygen adsorbates by steam electrolysis at 200° C. to 800° C. using an electrolysis cell comprising a solid electrolyte which is made of a proton-conducting ceramic, said electrolyte being arranged between an anode and a cathode, said anode and cathode each comprising a proton-conducting ceramic and the ratio of the electroactive surface to the geometric surface of each of which is equal to at least 10, said method comprising the following steps:

circulating a current between the anode and the cathode, wherein the density of the current is no less than 500 mA/cm²;

inserting water in the form of steam, which is fed under pressure to the anode;

oxidizing said water in the form of steam at the anode;

generating highly reactive oxygen at the anode after said oxidation;

generating protonated species in the electrolyte after said oxidation;

migrating said protonated species in the electrolyte;

reducing said protonated species at the surface of the cathode in the form of reactive hydrogen atoms.

2. Method according to claim 1, wherein said ratio between the electroactive surface and the geometric surface of said cathode and anode is no less than 100.

3. Method according to claim 1, wherein said density of the current is no less than 1 A/cm².

4. Method according to claim 1, wherein the partial and relative pressure of the steam is advantageously no less than 1 bar and preferentially no less than 10 bars.

5. Method according to claim 1, wherein the circulation of the current takes place between an anode and a cathode each made of a cermet constituted of a mixture of a proton-conducting ceramic and a conducting material.

6. Method according to claim 1, wherein said conducting material is a passivable material with high melting point being able to contain at least 40% of chromium.

7. Method according to claim 1, wherein the circulation of the current takes place between an anode and a cathode each comprising a proton-conducting ceramic formed of a perovskite doped with a lanthanide with one or more degrees of oxidation.

8. Method according to claim 1, wherein it comprises the following steps:

introducing carbon dioxide CO₂ and/or carbon monoxide CO at the cathode of the electrolysis cell;

reducing the CO₂ and/or CO introduced at the cathode from said generated reactive hydrogen atoms;

forming compounds of C_xH_yO_z type, where x≥1, 0<y≤(2x+2) and 0≤z≤2x after the reduction of the CO₂ and/or CO.

9. Method according to claim 1, wherein it comprises the following steps:

introducing nitrogen containing compounds at the cathode of the electrolysis cell;

reducing said nitrogen containing compounds introduced at the cathode from said generated reactive hydrogen atoms.

10. Method according to claim **1**, wherein said nitrogen containing compounds are compounds of the NO_x type where $x \geq 1$, said method comprising a step of forming compounds of $\text{N}_t\text{O}_y\text{H}_z$ type, where t is no less than 1, y no less than 0 and z no less than zero, after the reduction of the NO_x .

11. Method according to claim **9** wherein said nitrogen containing compounds are N_2 compounds, said method comprising a step of forming compounds of N_xH_y type where $x \geq 1$ and $y \geq 0$ to result in the formation of NH_3 after the reduction of N_2 .

12. Method according to claim **1**, wherein said reactive hydrogen atoms are used to carry out a step of hydrocracking at the cathode.

13. Method according to claim **1**, wherein said reactive hydrogen atoms are used to convert aromatic compounds at the cathode.

14. Method according to claim **1**, further comprising a step consisting in making said highly reactive oxygen react with a compound introduced at the anode such that the latter undergoes oxygenation.

15. Electrolysis cell for the implementation of the method according to claim **1** comprising:

a solid electrolyte, which is made of a proton-conducting ceramic;

an anode comprising a proton-conducting ceramic, said anode and cathode each having a ratio between the electroactive surface and the geometric surface equal to at least 10;

a cathode comprising a proton-conducting ceramic, said electrolyte being arranged between said anode and said cathode;

means for inserting water in the form of steam which is fed under pressure at the anode;

means for inducing a current circulating between the anode and the cathode, wherein the density of the current is no less than 500 mA/cm^2 .

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