US 20140284220A1

(19) **United States**

(12) **Patent Application Publication**

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**

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(21) Appl. No.: **14/350,844**

(22) PCT Filed: **Oct. 11, 2012**

(86) PCT No.: **PCT/EP2012/070214**

§ 371 (c)(1),
(2), (4) Date: **Apr. 10, 2014**

(30) **Foreign Application Priority Data**

Oct. 12, 2011 (FR) 1159221

Publication Classification

(51) **Int. Cl.**
C25B 1/04 (2006.01)

(52) **U.S. Cl.**
CPC *C25B 1/04* (2013.01)
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/cm^2; 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.

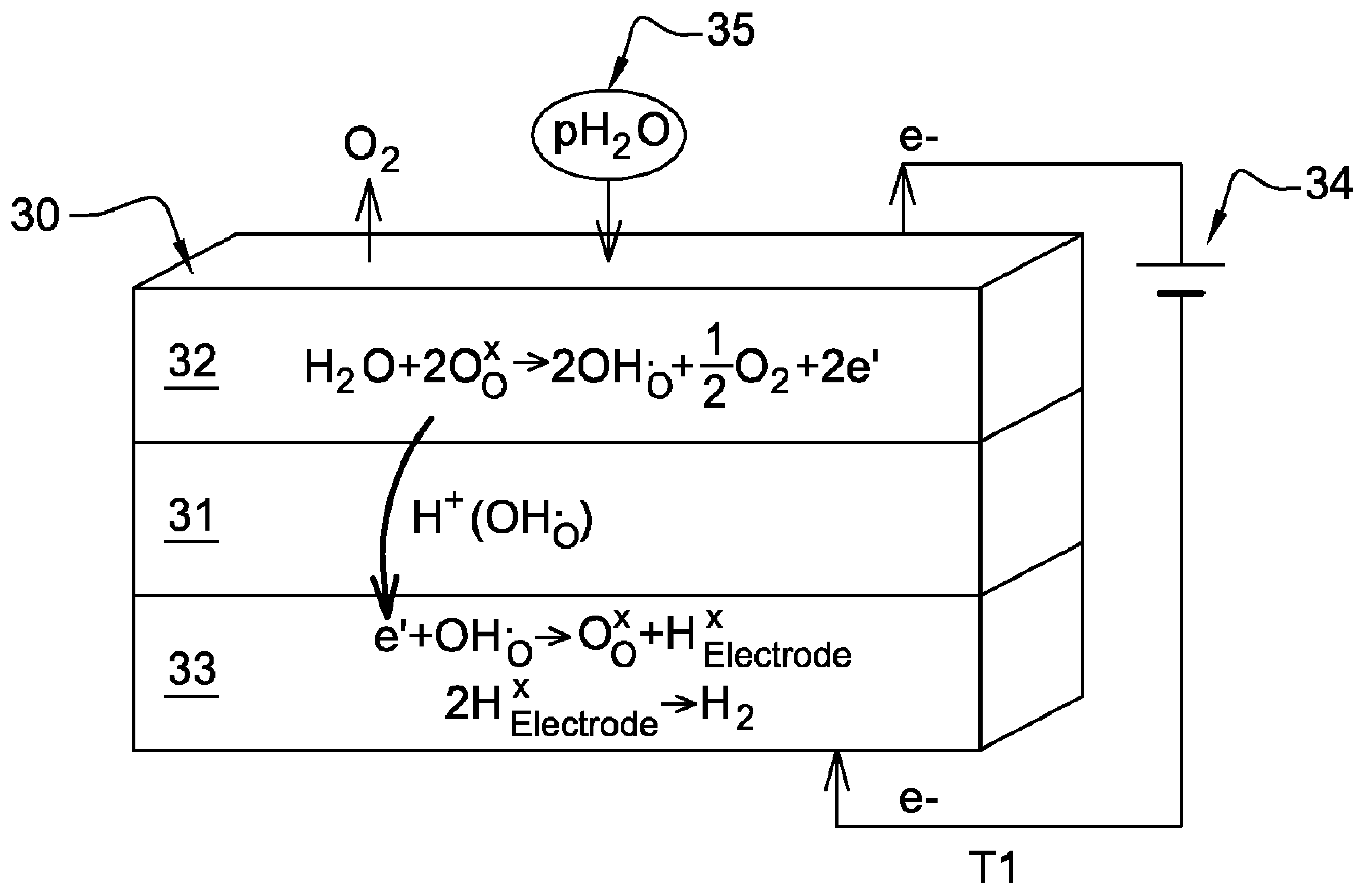


Fig. 1

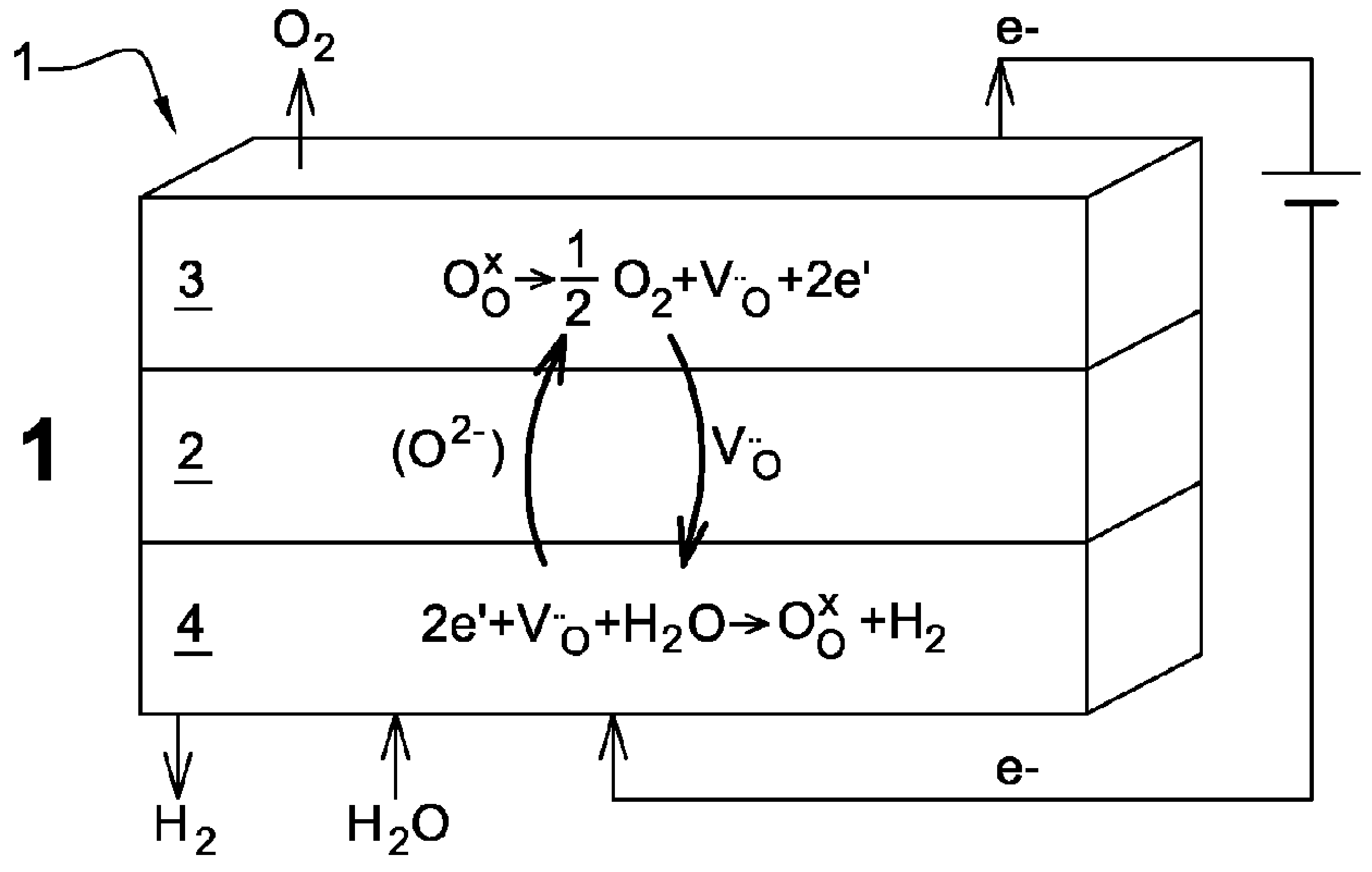


Fig. 2

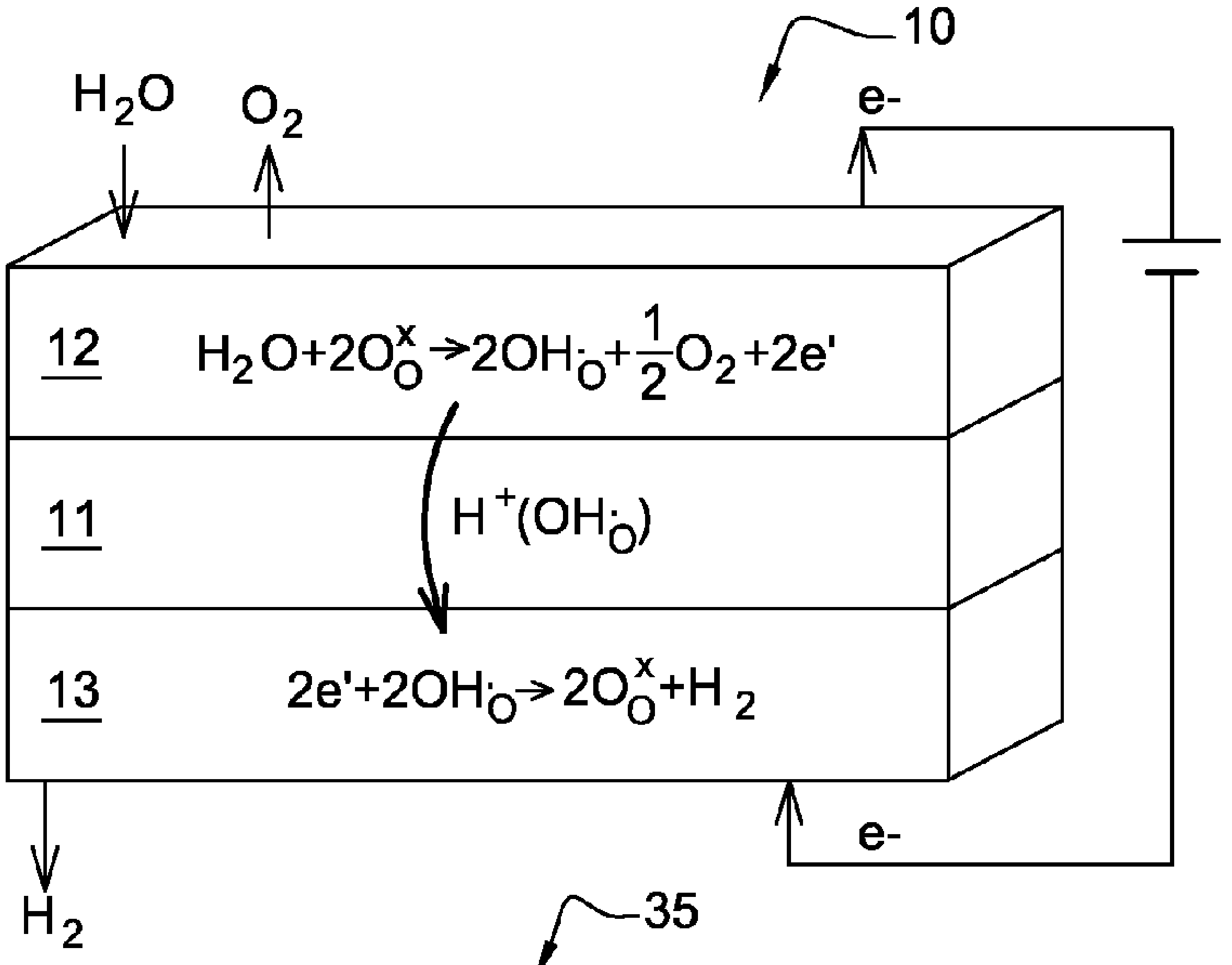
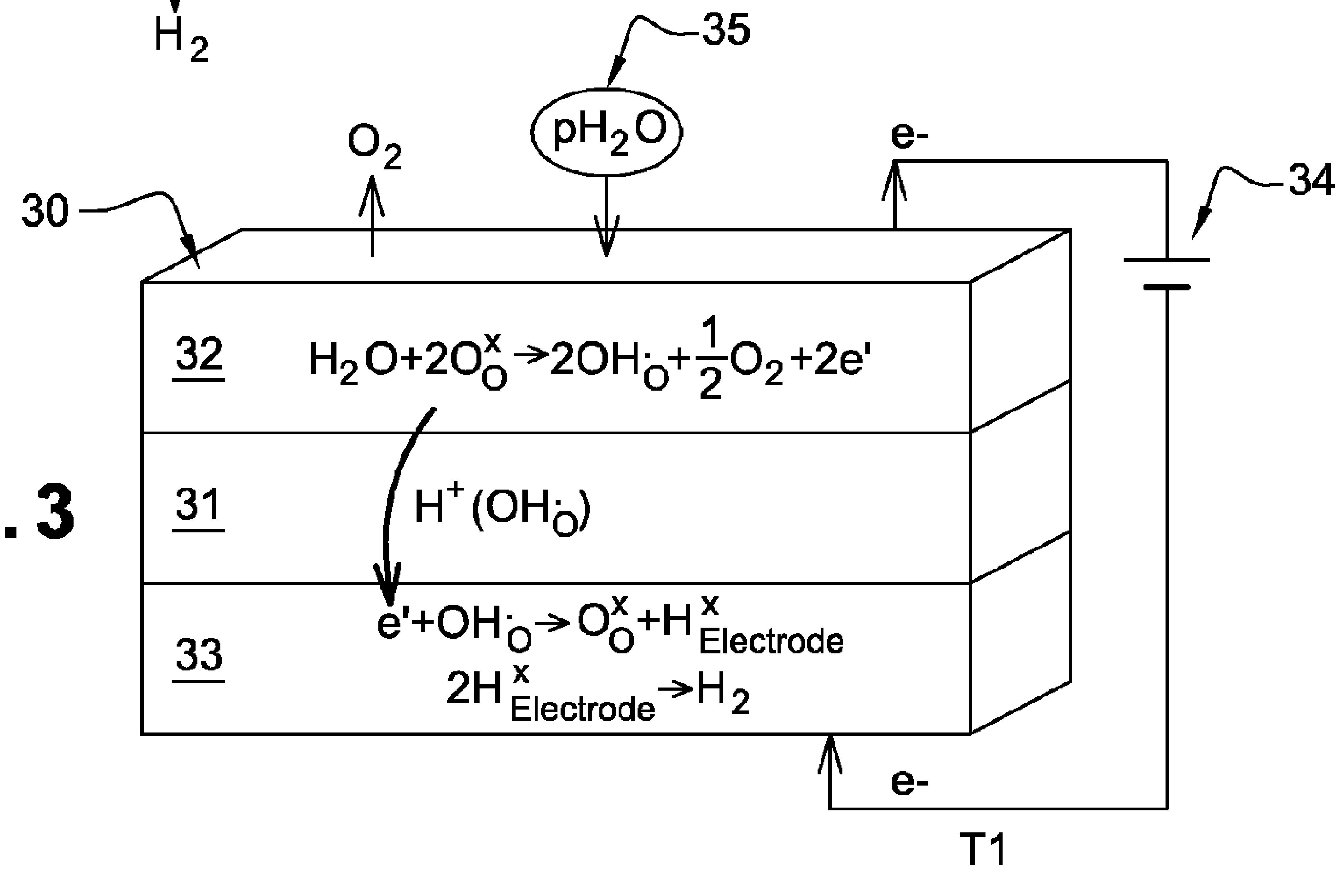


Fig. 3



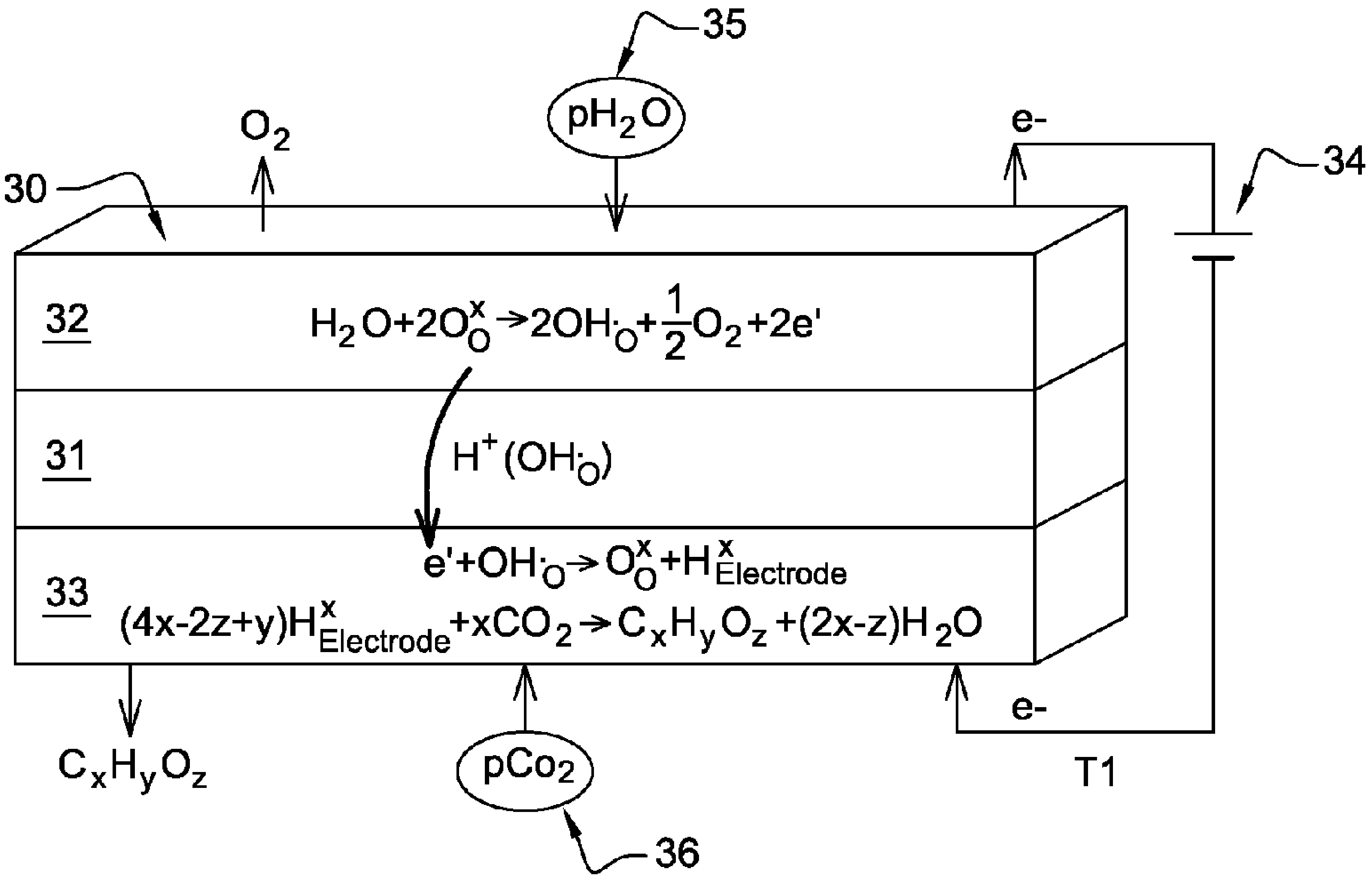

35
pH_2O
O_2
e-
34
30
32
$H_2O+2O_O^x \rightarrow 2OH_O^\cdot+\frac{1}{2}O_2+2e'$
31
$H^+(OH_O^\cdot)$
33
$e'+OH_O^\cdot \rightarrow O_O^x+H_{Electrode}^x$
$(4x-2z+y)H_{Electrode}^x+xCO_2 \rightarrow C_xH_yO_z+(2x-z)H_2O$
$C_xH_yO_z$
pCo_2
e-
T1
36

Fig. 4

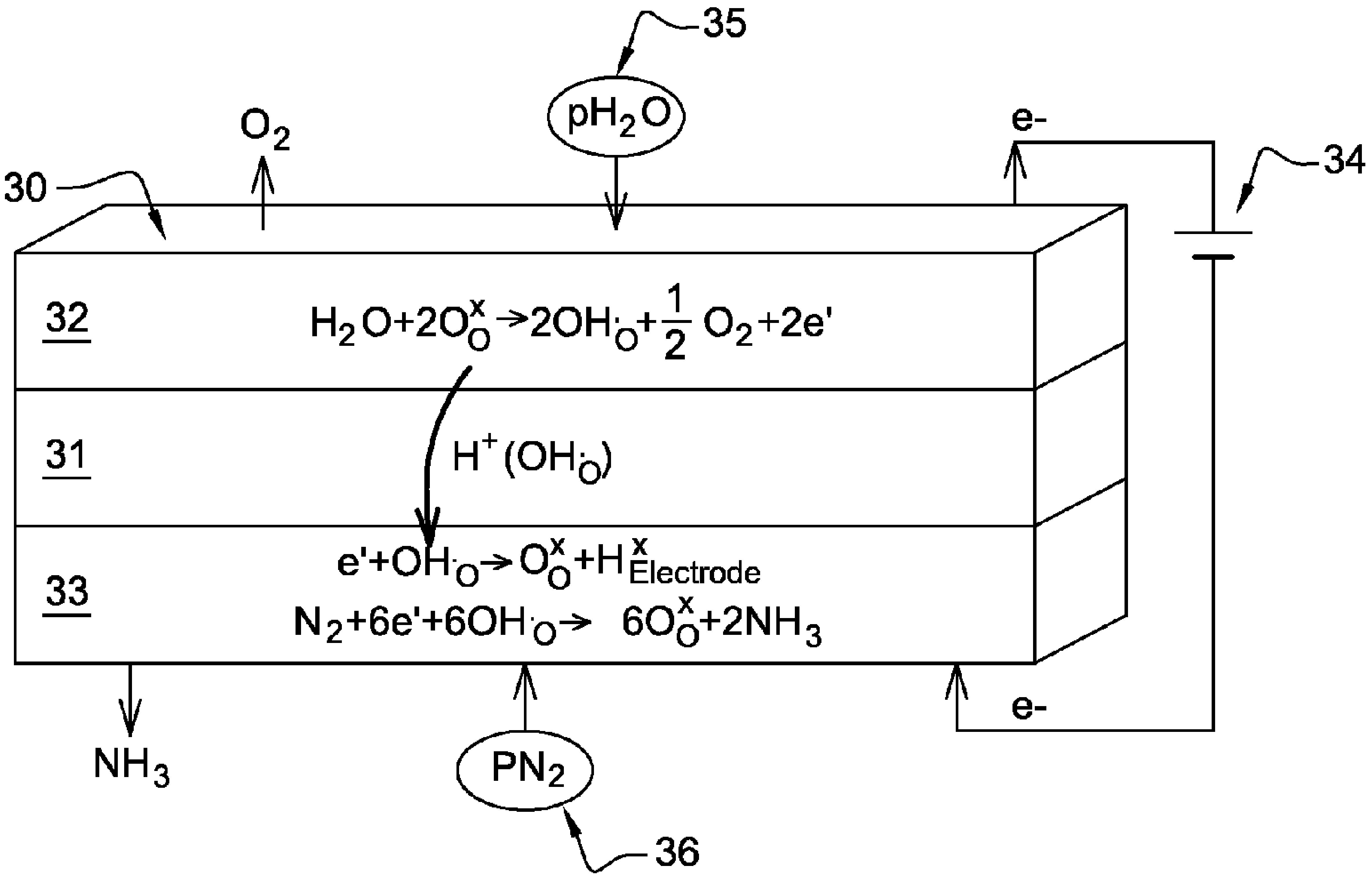

35
pH_2O
O_2
e-
34
30
32
$H_2O+2O_O^x \rightarrow 2OH_O^\cdot+\frac{1}{2}O_2+2e'$
31
$H^+(OH_O^\cdot)$
33
$e'+OH_O^\cdot \rightarrow O_O^x+H_{Electrode}^x$
$N_2+6e'+6OH_O^\cdot \rightarrow 6O_O^x+2NH_3$
NH_3
PN_2
e-
36

Fig. 6

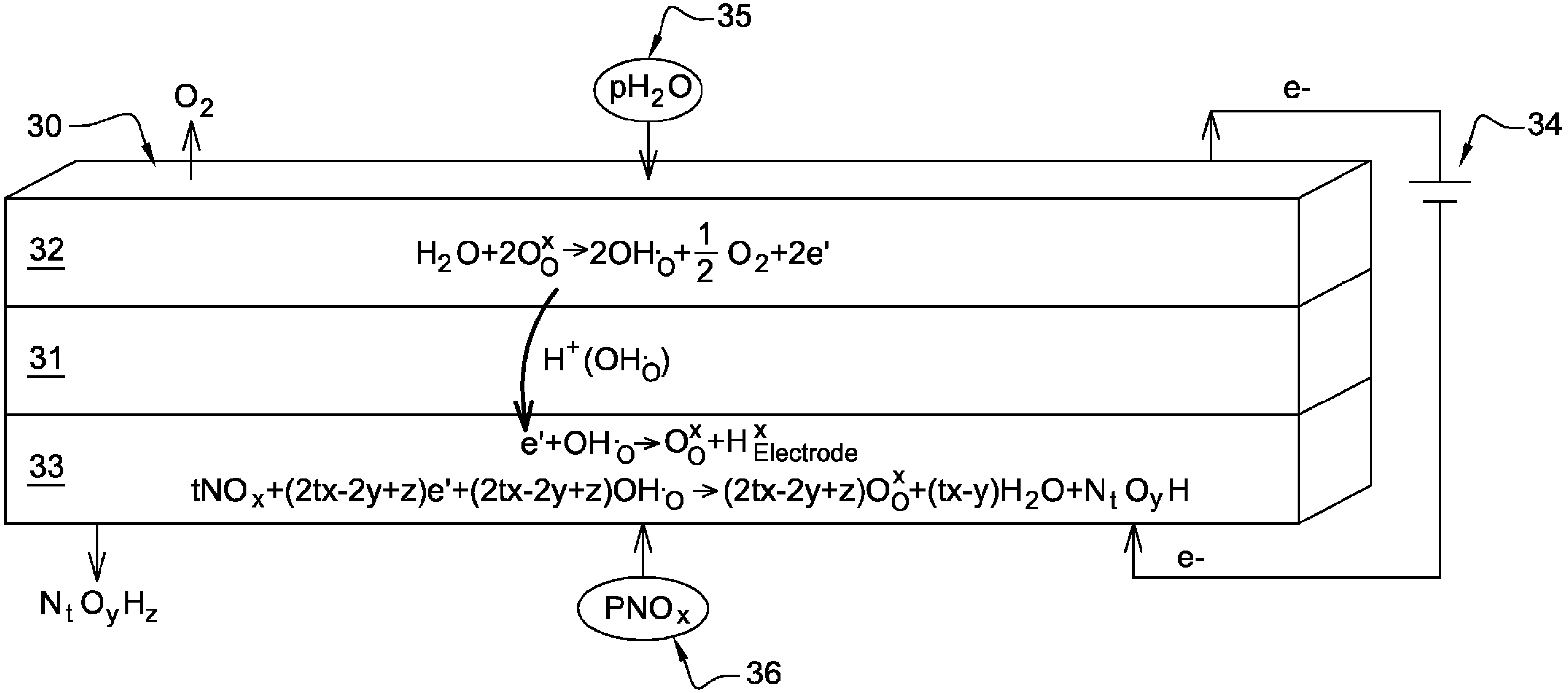

30
O_2
35
pH_2O
e-
34
32
$H_2O+2O_O^x \rightarrow 2OH^{\cdot}_O+\frac{1}{2}O_2+2e'$
31
$H^+(OH^{\cdot}_O)$
33
$e'+OH^{\cdot}_O \rightarrow O_O^x+H^x_{Electrode}$
$tNO_x+(2tx-2y+z)e'+(2tx-2y+z)OH^{\cdot}_O \rightarrow (2tx-2y+z)O_O^x+(tx-y)H_2O+N_tO_yH$
e-
$N_tO_yH_z$
PNO_x
36

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 (CO_2, CO) by electrochemical hydrogenation. Patent applications WO2008152317 and WO2009150352 describe examples of such methods.

[0003] Hydrogen (H_2) 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 CO_2 type. In fact, 8 to 10 tonnes of CO_2 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 anfractuosities 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 O^{2-} 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 O^{2-} 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 H_2O on the side of the cathode **4**. This reduction forms hydrogen H_2 and O^{2-} ions (O_O^X in the Kröger-Vink notation) at the surface of the cathode **4** according to the reaction:

$$2e'+V_{\ddot{O}}+H_2O \rightarrow O_O^X+H_2$$

[0013] The O^{2-} ions, more specifically the oxygen vacancies ($V_{\ddot{O}}$), migrate through the electrolyte **2** to form oxygen O_2 at the surface of the anode **3**, electrons e' being released according to the oxidation reaction:

$$O_O^X \rightarrow \tfrac{1}{2}O_2+V_{\ddot{O}}+2e'$$

[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 H_2O on the side of the anode **12**. The steam fed into the anode **12** is thus oxidised to form oxygen O_2 and H^+ ions (or $OH._O$ in the Kröger-Vink notation), this reaction releasing electrons e^- according to the equation:

$$H_2O+2O_O^X \rightarrow 2OH._O+\tfrac{1}{2}O_2+2e'$$

[0018] The H^+ ions (or $OH._O$ in the Kröger-Vink notation) migrate through the electrolyte **11**, to form hydrogen H_2 at the surface of the cathode **13** according to the equation:

$$2e'+2OH._O \rightarrow 2O_O^X+H_2$$

[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 H_2 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 $H_{Electrode}^X$ the Kröger-Vink notation). These species being highly reactive, they usually recombine to form hydrogen H_2 according to the equation:

$$2H_{Electrode}^X \rightarrow H_2$$

[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 O^{2-} 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/cm^2;
- **[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:

$$e'+OH._{O}\rightarrow O_{O}^{X}+H_{Electrode}^{X}$$

[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/cm^2;
- **[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 $C_xH_yO_Z$ 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 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 $N_tO_yH_z$ 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 electrolysers,

[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 formation 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 carburation.

[0094] 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 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:

$$H_2O+2O_O^X \rightarrow 2OH._O+\frac{1}{2}O_2+2e'$$

$$2e'+2OH._O \rightarrow 2O_O^X+H_2.$$

[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. Keddam, 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 $OH._O$ in the Kröger-Vink notation), this reaction releasing electrons e^- according to the equation:

$$H_2O+2O_O^X \rightarrow 2OH._O+\frac{1}{2}O_2+2e'$$

[0105] The H^+ ions (or $OH._O$ 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:

$$2e'+2OH._O \rightarrow 2O_O^X+H_2$$

[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 $H_{Electrode}^X$ in the Kröger-Vink notation). These species being highly reactive,

- **[0108]** either they recombine to form hydrogen H_2 according to the equation: $2H_{Electrode}^X \rightarrow H_2$ (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 $O_{Electrode}^X$ 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

H_2SO_4 or to form oxygen for the oxycombustion. One thus has for example the following equations:

$$H_2O+2O_O^X \rightarrow 2OH._O+O_{Electrode}^X+2e'$$

$$H_2O+SO_X+(3-x)O_{Electrode}^X \rightarrow H_2SO_4$$

$$O_{Electrode}^X \rightarrow \tfrac{1}{2}O_2$$

[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 CO_2 and/or CO.

[0114] The cell **30** of FIG. **3** further comprises means **36** making it possible to insert under pressure gas (pCO_2 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**, CO_2 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:

$$(6n+2)H_{Electrode}^X+nCO_2 \rightarrow C_nH_{2n+2}+2nH_2O$$

$$6nH_{Electrode}^X+nCO_2 \rightarrow C_nH_{2n}+2nH_2O$$

$$6nH_{Electrode}^X+nCO_2 \rightarrow C_nH_{2n+2}O+(2n-1)H_2O$$

$$(6n-2)H_{Electrode}^X+nCO_2 \rightarrow C_nH_{2n}O+(2n-1)H_2O$$

[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:

$$(4x-2z+y)H_{Electrode}^X+xCO_2 \rightarrow C_xH_yO_Z+(2x-z)H_2O$$

[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 CO_2 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 N_2. 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 CO_2. 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: $e'+OH._O \rightarrow O_O^X+H_{Electrode}^X$.

[0130] Consequently, in the presence of NO_X on the catholic 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:

$$tNO_x+(2tx-2y+z)H_{Electrode}^X. \rightarrow (tx-y)H_2O+N_tO_yH_z.$$

[0131] As an example, these compounds are either NO_y less oxidised than the NO_x compounds fed in under pressure, nitrogen N_2, or ammonia NH_3.

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

$$H_2O+2O_O^X \rightarrow 2OH._O+\tfrac{1}{2}O_2+2e' \qquad \text{(anode 32)}$$

$$tNO_x+(2tx-2y+z)e'+(2tx-2y+z)OH._O \rightarrow (2tx-2y+z)O_O^X+(tx-y)H_2O+N_tO_yH_z \qquad \text{(cathode 33).}$$

[0133] The solution according to the invention makes it possible to reduce the number of reactors required for the reduction of NOx 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 N_2. 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 NH_3.

[0135] The cell **30** of FIG. **3** further comprises means **36** making it possible to insert nitrogen N_2 under pressure into the cathodic compartment **33**.

[0136] The problem is here to produce in massive quantity, at low cost and without emission of CO_2, ammonia, by electro-catalytic hydrogenation of N_2.

[0137] At present, ammonia is produced by catalytic hydrogenation reaction of N_2 during steam reforming of hydrocarbons. The synthesis of this product thus indirectly emits CO_2. In addition, the synthesis method induces a very great volatility of the production price of NH_3. In fact 80% of the price of NH_3 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: $e'+OH._{O}\rightarrow O_{O}^{X}+H_{Electrode}^{X}$.

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

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

$$H_2O+2O_{O}^{X}\rightarrow 2OH._{O}+\tfrac{1}{2}O_2+2e'$$

$$N_2+6e'+6OH._{O}\rightarrow 6O_{O}^{X}+2NH_3$$

[0143] The solution of FIG. **6** makes it possible to reduce the number of reactors required for the production of NH_3 (which serves as H_2 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 CO_2.

[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 H_2 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/cm^2;

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/cm^2.

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 CO_2 and/or carbon monoxide CO at the cathode of the electrolysis cell;

reducing the CO_2 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 CO_2 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 $N_tO_yH_z$ 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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