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(54) **CHEMICAL/ELECTROCHEMICAL PROTON CERAMIC MEMBRANE REACTOR**

(57) The present disclosure relates to a chemical/electrochemical proton ceramic membrane reactor for promote hydrogenation and de-hydrogenation reactions.

It is disclosed a chemical/electrochemical proton ceramic membrane reactor for promoting hydrogenation and de-hydrogenation reactions, in particular direct hydrogenation/de-hydrogenation of amines, at temperatures equal or lower than 700°C comprising a proton ceramic electrochemical cell containing a molten hydroxide catholyte and a cathode fraction; a ceramic protonic

electrolyte membrane comprising  $A_z(B'_{1-x}B''_x)_{1-y}M_yO_{3-\delta}$ , wherein A, B', B'', M are independently selected from each other; A is selected from a list consisting of Ba<sup>2+</sup>, Sr<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, or their combination; B' and B'' are selected from a list consisting of Zr<sup>4+</sup>, Ce<sup>4+</sup>, Sn<sup>4+</sup>, Hf<sup>4+</sup>, Mn<sup>4+</sup>, Ru<sup>4+</sup>, Pd<sup>4+</sup>, Ir<sup>4+</sup>, Pb<sup>4+</sup>, or their combination; M is selected from a list consisting of Y<sup>3+</sup>, La<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, Dy<sup>3+</sup>, Yb<sup>3+</sup>, or their combination, and z varies from 0.8 to 1, x varies between 0 to 1, y varies between 0 and 0.5, and  $\delta$  varies from 0 to 2.

## Description

## TECHNICAL FIELD

**[0001]** The present disclosure relates to a chemical/electrochemical proton ceramic membrane reactor for promote hydrogenation and de-hydrogenation reactions.

## BACKGROUND

**[0002]** Proton ceramic membrane reactors (PCMRs) are among the most promising and efficient technologies to convert electrical energy into useful gaseous chemical substances. This type of device is an electrochemical reactor that includes two electrodes, an anode and cathode, that are connected to an external electric circuit and that are separated by an electrolyte membrane. The electrolyte membrane is an electronic insulator, *i.e.*, impermeable to electrons and it is permeable only to ions resultant from the oxidation and reduction reactions that take place at the electrodes. The constituent ions of the electrolyte promote the ionic transport between cathode and anode.

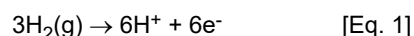
**[0003]** The anode is powered by the gas fuel, for example  $H_2$ ,  $H_2O$ , or hydrocarbons, where it is oxidized, and the cathode is powered by oxygen or nitrogen,  $O_2$  or  $N_2$ , where it is reduced. Electrons move towards the cathode by means of an external circuit, and the protons move from the anode to the cathode. The electrodes are electronic conductors and they are also catalytically active for the oxidation/reduction reactions. Since the reactants need to reach the active sites responsible for the electrochemical promotion of each reaction, *e.g.*, reduction, oxidation, and cannot be mixed, the electrodes are porous, and the electrolyte is dense.

**[0004]** On this respect, document US 2005/0064259 A1 describes an invention including a fuel cell reactor using a protonic ceramic membrane using barium cerate-based proton conductors,  $BaCe_{1-x}Y_xO_{3-\delta}$  (BCY), for the simultaneous production of water and electricity. Owing to its very high equilibrium constant for hydration, BCY electrolytes are reported to achieve some of the highest proton conductivities, *i.e.*,  $\sim 10^{-3} \text{ S cm}^{-1}$  at  $400^\circ\text{C}$ , under humidified fuels,  $p_{H_2O} \sim 10^{-5} - 10^{-2} \text{ atm}$ , among other proton-conducting ceramics [1,2]. This characteristic is highly interesting for electrochemical processes involving hydrogenation or dehydrogenation reactions [2].

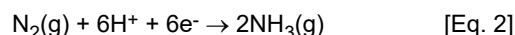
**[0005]** Due to the flexibility of fuel choices, a PCMR can be used for the synthesis of value-added chemical products *viz.* hydrogen ( $H_2$ ), ammonia ( $NH_3$ ) synthesis, and hydrogenation/de-hydrogenation of any member of a family of nitrogen-containing organic compounds.

**[0006]** In the case of ammonia, the electrochemical synthesis consists of the conversion of a hydrogen source, such as  $H_2$ ,  $H_2O$ , or a hydrocarbon, and nitrogen ( $N_2$ ), yielding ammonia in gaseous form. Studies on the electrochemical synthesis of ammonia using PCMRs relate to the beginning of the 20th century. For example, Marnellos & Stoukides [3] disclosed an electrochemical membrane reactor based on a strontia-ceria-ytterbia (SCY) perovskite solid state proton ( $H^+$ ) conductor, where ammonia could be synthesized at the surface of a porous metal cathode made of a polycrystalline palladium film. This process can operate under ambient pressure and at  $570^\circ\text{C}$ .

**[0007]** In contrast to the Haber-Bosch process, ammonia can be formed from renewable sources, such as water and air, without the liberation of carbon dioxide by using a PCMR. In this approach, a ceramic electrochemical cell is used, being composed of an electrolyte membrane and two adjacent electrodes, one on each side of the membrane. The membrane allows to separate gaseous reactants from both electrode sides, being permeable only to protons,  $H^+$  species, produced by *in situ* dehydrogenation into protons and electrons at the anode side:

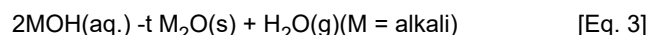


**[0008]** Protons will then diffuse towards the cathode electrode, on applying an electrical potential between the cathode and the anode, where they will finally react with  $N_2$ , from air dissociation, to form ammonia [4],



**[0009]** Nonetheless, in the cathode, one of the major limitations is related to the dissociation of  $N_2$  molecule [5], leading to the unwanted competing reaction of  $H_2$  evolution (HER) at the cathode [6,7]. Therefore, current limitations are to find suitable electrocatalyst materials with increased selectivity toward  $N_2$  molecule dissociation [8].

**[0010]** In this regard, recent studies using molten hydroxide materials have disclosed the capability of these materials to conduct ionic species resulting from the dissociation of  $N_2$  using  $Fe_2O_3$  nanocatalysts [9]. However, one of the main limitations of these melts is related to the continuous deprotonation of the molten hydroxide with ammonia formation:



[0011] These facts are disclosed in order to illustrate the technical problem addressed by the present disclosure.

## GENERAL DESCRIPTION

[0012] The present disclosure relates to a chemical/electrochemical proton ceramic membrane reactor for promote hydrogenation and de-hydrogenation reactions.

[0013] The present disclosure comprises a chemical/electrochemical proton ceramic membrane reactor (PCMR) to promote hydrogenation and de-hydrogenation reactions at temperatures equal or lower than 700°C. In particular, this is a novel intermediate temperature membrane reactor for direct hydrogenation/de-hydrogenation of amines, namely for the synthesis of ammonia.

[0014] The technology described in this current invention intends to address the problem existing in the prior art related to the continuous deprotonation of the molten hydroxide with ammonia formation by the innovative integration of a molten hydroxide catholyte into a PCMR. In this way, the protonic transport through the electrolyte membrane will be able to continuously supply  $H^+$  species to the melt, which mitigates hydroxide decomposition (Eq. (1)). Nonetheless, this combination offers another critical advantage since both  $H^+$  and  $N^-$  species are able to diffuse through the hydroxide melt [9,10]. Hence, the need for charge-transfer during  $NH_3$  formation can be avoided as the  $N_2$  reduction reaction will take place at the solid electrocatalyst electrode, while the  $NH_3$  formation reaction can proceed inside the molten hydroxide solution. This ground-breaking solution leads to improving reaction selectivity by suppressing hydrogen evolution reaction (HER), an essential electrocatalytic criterion for the current process [11].

[0015] An aspect of the present disclosure involves the use of  $A_z(B'_{1-x}B''_x)_{1-y}M_yO_{3-\delta}$ -based membrane - as a ceramic protonic electrolyte membrane, herein designated as PE, wherein A is selected from a list consisting of  $Ba^{2+}$ ,  $Sr^{2+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , or their combination; B' and B'' are selected from a list consisting of  $Zr^{4+}$ ,  $Ce^{4+}$ ,  $Sn^{4+}$ ,  $Hf^{4+}$ ,  $Mn^{4+}$ ,  $Ru^{4+}$ ,  $Pd^{4+}$ ,  $Ir^{4+}$ ,  $Pb^{4+}$ , or their combination; M is selected from a list consisting of  $Y^{3+}$ ,  $La^{3+}$ ,  $Nd^{3+}$ ,  $Sm^{3+}$ ,  $Eu^{3+}$ ,  $Gd^{3+}$ ,  $Dy^{3+}$ ,  $Yb^{3+}$ , or their combination; z ranges from 0.8 to 1; x ranges from 0 to 1, y ranges from 0 to 0.5 and  $\delta$  ranges from 0 to 2.

[0016] Namely, the use of ceramic protonic electrolyte membrane to operate under:

- humidity conditions comprising a water vapor partial pressure range of  $10^{-7} \text{ atm} \leq p_{H_2O} \leq 10^{-2} \text{ atm}$ , preferably of  $10^{-6} \text{ atm} \leq p_{H_2O} \leq 10^{-3} \text{ atm}$ , more preferable of  $10^{-5} \text{ atm} \leq p_{H_2O} \leq 10^{-4} \text{ atm}$ ;

- temperatures equal or lower than 700°C, preferably from 400°C to 670°C, more preferable from 450°C to 550°C.

[0017] In an embodiment for better results, the ceramic protonic electrolyte membrane is BaCeOs or BaZrOs, or mixtures thereof, optionally doped by further acceptor dopants Sn, Gd or Y.

[0018] In an embodiment for better results, the ceramic protonic electrolyte membrane is in the micrometer range of thickness, preferable below 100  $\mu\text{m}$ , more preferably below 40  $\mu\text{m}$ .

[0019] Another aspect of the present disclosure involves the use of a molten hydroxide salt, *i.e.*, binary phases of alkali-hydroxide compositions  $A'_{1-x}A''_x(\text{OH})$  catholytes, herein designated as MHS ("molten hydroxide salt"), wherein, A' and A'' are selected from a list consisting of  $Na^+$ ,  $K^+$ ,  $Ba^{2+}$ ,  $Sr^{2+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ; x varies between 0 to 1.

[0020] Namely, the use of molten hydroxide salt to operate under:

- humidity conditions comprising a water vapor partial pressure range of  $10^{-7} \text{ atm} \leq p_{H_2O} \leq 10^{-2} \text{ atm}$ , preferably of  $10^{-6} \text{ atm} \leq p_{H_2O} \leq 10^{-3} \text{ atm}$ , more preferable of  $10^{-5} \text{ atm} \leq p_{H_2O} \leq 10^{-4} \text{ atm}$ ;

- temperatures equal or lower than 700°C, preferably between 400°C and 670°C, more preferable between 450°C and 550°C;

powder, porous, or molten form, or mixtures thereof.

[0021] Another aspect of the present disclosure involves the use of a composite porous anode, which comprises a metal-fraction (conductor of electrons) and a ceramic-fraction (conductor of protons), herein designated as cermet, wherein,

[0022] The metal-fraction is a doped metal or metal oxide with at least one element selected from a list consisting of: scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, hafnium, tantalum, tungsten, iridium, platinum, gold, or mixtures thereof;

[0023] The ceramic-fraction is composed by the ceramic protonic electrolyte membrane

[0024] Namely, the use of the composite porous anode to operate under:

humidity conditions comprising a water vapor partial pressure range of  $10^{-7} \text{ atm} \leq p_{\text{H}_2\text{O}} \leq 10^{-2} \text{ atm}$ , preferably of  $10^{-6} \text{ atm} \leq p_{\text{H}_2\text{O}} \leq 10^{-3} \text{ atm}$ , more preferable of  $10^{-5} \text{ atm} \leq p_{\text{H}_2\text{O}} \leq 10^{-4} \text{ atm}$ ;

temperatures equal or lower than  $700^\circ\text{C}$ , preferably between  $400^\circ\text{C}$  and  $670^\circ\text{C}$ , more preferable between  $450^\circ\text{C}$  and  $550^\circ\text{C}$ .

**[0025]** In one embodiment, the composite porous anode includes porosity is below 40%, preferably between 10% and 30%, as determined by Scanning Electron Microscopy (SEM), and the pore size is below  $100 \mu\text{m}$ , preferably between  $10 \mu\text{m}$  and  $50 \mu\text{m}$ , as determined by gas pycnometry.

**[0026]** For best results from the membrane electrode assembly (MEA), the anode metal may be nickel, nickel oxide or mixtures thereof.

**[0027]** Another aspect of the present disclosure involves the use of a composite cathode, which comprises a metal-fraction (conductor of electrons) and a molten hydroxide salt-fraction (conductor of protons and nitrogen ions), herein designated as cathode, wherein, the metal-fraction is a doped metal or metal oxide with at least one element from the following list: scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, hafnium, tantalum, tungsten, iridium, platinum, gold, or mixtures thereof.

**[0028]** The salt-fraction is composed by the molten hydroxide salt.

**[0029]** Namely, the use of the composite porous anode to operate under:

humidity conditions comprising a water vapor partial pressure range of  $10^{-7} \text{ atm} \leq p_{\text{H}_2\text{O}} \leq 10^{-2} \text{ atm}$ , preferably of  $10^{-6} \text{ atm} \leq p_{\text{H}_2\text{O}} \leq 10^{-3} \text{ atm}$ , more preferable of  $10^{-5} \text{ atm} \leq p_{\text{H}_2\text{O}} \leq 10^{-4} \text{ atm}$ ;

temperatures equal or lower than  $700^\circ\text{C}$ , preferably between  $400^\circ\text{C}$  and  $670^\circ\text{C}$ , more preferable between  $450^\circ\text{C}$  and  $550^\circ\text{C}$ .

**[0030]** In an embodiment for best results, for the cathode, the metal-fraction may be iron, iron oxide or mixtures thereof.

**[0031]** In one embodiment of the present invention, the membrane electrode assembly (MEA) includes:

the ceramic protonic electrolyte membrane, which is an electronic insulator, allowing the permeation of predominantly protons, located between the anode and the cathode, impermeable to both gaseous reactants and products of hydrogenation and dehydrogenation reactions;

the composite porous anode, which comprises a metal fraction (conductor of electrons) and a ceramic-fraction (ceramic protonic electrolyte membrane); where the anode is capable of operating at temperatures equal or lower than  $700^\circ\text{C}$ , preferably between  $400^\circ\text{C}$  and  $670^\circ\text{C}$ , more preferable between  $450^\circ\text{C}$  and  $550^\circ\text{C}$ ;

the composite cathode, which comprises a metal fraction (conductor of electrons) and a molten hydroxide salt phase, herein designated as molten hydroxide salt (MHS).

**[0032]** Another aspect of the present invention is related to a chemical/electrochemical membrane reactor to promote hydrogenation and dehydrogenation reactions. In particular, for the direct dehydrogenation/dehydrogenation of amines, namely for the synthesis of ammonia. This reactor comprises,

at least one membrane electrode assembly (MEA) as previously described in this disclosure;

an anode chamber, where the feed stream is composed of a hydrogen-containing gas, preferably hydrogen, nitrogen, argon, or mixtures thereof, and where the oxidation of hydrogen to protons occurs;

a cathode chamber, where the feed stream is composed by a nitrogen-containing gas, and where the reduction of nitrogen occurs; and, where an inert gas, preferably nitrogen, hydrogen, or mixtures thereof, is introduced;

a power supply that directly connects the two electrodes (anode and cathode) of the membrane electrode assembly (MEA) and imposes a difference of electric potential between both; the range of the applied difference of potential is from  $-0.2 \text{ V}$  to  $-2 \text{ V}$ , more preferably from  $-0.5 \text{ V}$  to  $-1 \text{ V}$ ; nonetheless, the optimal difference of potential will strongly depend on the operating conditions (for example, temperature, pressure, concentration of chemical reactants, etc.).

**[0033]** It is disclosed a chemical/electrochemical proton ceramic membrane reactor for promote hydrogenation and de-

hydrogenation reactions, in particular direct hydrogenation/de-hydrogenation of amines, at temperatures equal or lower than 700°C comprising: a proton ceramic electrochemical cell containing a molten hydroxide catholyte and a cathode fraction; a ceramic protonic electrolyte membrane comprising  $A_z(B'_{1-x}B''_x)_{1-y}M_yO_{3-\delta}$  wherein A, B', B'', M are independently selected from each other; A is selected from a list consisting of Ba<sup>2+</sup>, Sr<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, or their combination; B' and B'' are selected from a list consisting of Zr<sup>4+</sup>, Ce<sup>4+</sup>, Sn<sup>4+</sup>, Hf<sup>4+</sup>, Mn<sup>4+</sup>, Ru<sup>4+</sup>, Pd<sup>4+</sup>, Ir<sup>4+</sup>, Pb<sup>4+</sup>, or their combination; M is selected from a list consisting of Y<sup>3+</sup>, La<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, Dy<sup>3+</sup>, Yb<sup>3+</sup>, or their combination; z ranges from 0.8 to 1; x ranges from 0 to 1; y ranges from 0 to 0.5;  $\delta$  ranges from 0 to 2.

**[0034]** In an embodiment, the ceramic protonic electrolyte membrane used in the chemical/electrochemical proton ceramic membrane reactor is selected from a list consisting of BaCeOs, BaZrO<sub>3</sub>, or their combinations.

**[0035]** In an embodiment, the ceramic protonic electrolyte membrane used in the chemical/electrochemical proton ceramic membrane reactor is doped, preferably doped with Sn, Gd or Y.

**[0036]** In an embodiment, the chemical/electrochemical proton ceramic membrane reactor has Y<sup>3+</sup> as M.

**[0037]** In an embodiment, the thickness of the ceramic protonic electrolyte membrane used in the chemical/electrochemical proton ceramic membrane reactor is below 100  $\mu$ m, preferably below 40  $\mu$ m.

**[0038]** In an embodiment, the molten hydroxide catholyte used in the chemical/electrochemical proton ceramic membrane reactor is a binary phase of alkali-hydroxide composition A'<sub>1-x</sub>A''<sub>x</sub>(OH) catholyte, wherein A' and A'' are independently selected from each other; A' and A'' are selected from a list consisting of Na<sup>+</sup>, K<sup>+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>; x varies between 0 to 1.

**[0039]** In an embodiment, the binary phases of alkali-hydroxide compositions A'<sub>1-x</sub>A''<sub>x</sub>(OH) catholytes used in the chemical/electrochemical proton ceramic membrane reactor are in the form of powder, porous, or molten form, or mixtures thereof.

**[0040]** In an embodiment, the ceramic protonic electrolyte membrane used in the chemical/electrochemical proton ceramic membrane reactor operates at temperatures from 400°C to 670°C, preferably from 450°C to 550°C.

**[0041]** In an embodiment, the ceramic protonic electrolyte membrane of the chemical/electrochemical proton ceramic membrane reactor operates at a water vapor partial pressure range from 10<sup>-7</sup> atm to 10<sup>-2</sup> atm, preferably from 10<sup>-6</sup> atm to 10<sup>-3</sup> atm, more preferably from 10<sup>-5</sup> atm to 10<sup>-4</sup> atm.

**[0042]** In an embodiment, the chemical/electrochemical proton ceramic membrane reactor further comprises a composite porous anode comprising a metal-fraction and a ceramic-fraction.

**[0043]** In an embodiment, the porosity of the composite porous anode used in the chemical/electrochemical proton ceramic membrane reactor is below 40%, preferably between 10% and 30%, as determined by Scanning Electron Microscopy (SEM), and the pore size is below 100  $\mu$ m, preferably between 10  $\mu$ m and 50  $\mu$ m, as determined by gas pycnometry.

**[0044]** In an embodiment, the cathode fraction used in the chemical/electrochemical proton ceramic membrane reactor comprises a metal-fraction and a molten hydroxide salt-fraction.

**[0045]** In an embodiment, the metal-fraction used in the chemical/electrochemical proton ceramic membrane reactor is a doped metal or metal oxide with at least one element selected from a list consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, hafnium, tantalum, tungsten, iridium, platinum, gold, or mixtures thereof.

**[0046]** In an embodiment, the chemical/electrochemical proton ceramic membrane reactor further comprises an anode chamber, preferably composed of a hydrogen-containing gas, wherein the hydrogen-containing gas is selected from a list consisting of hydrogen, nitrogen, argon, or mixtures thereof.

**[0047]** In an embodiment, the chemical/electrochemical proton ceramic membrane reactor further comprises a cathode chamber, preferably composed of a nitrogen-containing gas, wherein the nitrogen-containing gas is selected from a list consisting of nitrogen, hydrogen, or mixtures thereof.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0048]** The following figures provide preferred embodiments for illustrating the disclosure and should not be seen as limiting the scope of invention.

**Figure 1:** Schematic representation of the proton ceramic membrane reactor working principle.

**Figure 2:** Photographic representation of an embodiment of the top-view surface of the Ni-BCY cermet anode.

**Figure 3:** Photographic representation of an embodiment of the top-view surface of the BCY protonic electrolyte.

**Figure 4:** Photographic representation of an embodiment of the cross-section of a Fe<sub>2</sub>O<sub>3</sub>-(Na,K)OH composite cathode film.

**Figure 5:** Schematic representation of an embodiment of a membrane electrode assembly.

**Figure 6:** Photographic representation of an embodiment of the cross-section of a (Na,K)OH-BCY interface.

**Figure 7:** Schematic representation of an embodiment of a membrane electrode assembly.

## DETAILED DESCRIPTION

**[0049]** The present disclosure relates to a chemical/electrochemical proton ceramic membrane reactor for promote hydrogenation and de-hydrogenation reactions.

**[0050]** In the present disclosure, one solution includes the fabrication of the membrane electrode assembly (MEA), which will be explained in the following embodiments.

Membrane electrode assembly (MEA)

**[0051]** The present application discloses a process to prepare the anode supported MEA by a spin-coating method, which comprises the following steps:

obtaining an anode by mixing a metallic and electronic conductor catalyst with a protonic ceramic (*i.e.*, PE) and an organic additive; the proportion of metal oxide on the ions conductor ranges from 30% to 70% (w/w), and the concentration of organic additive - preferably starch or polyvinyl alcohol - in the mixture, ranges between 5% to 30% (w/w) - preferably between 10% and 20% (w/w) in the presence or absence of a solvent;

shaping the resulting mixture, anode support (1), into a mold and pressing;

pre-sintering of the anode support (1) in the temperature range 800°C to 1000°C, preferably between 900°C and 1000°C, for 1 h to 2 h, with a heating rate between 1 °C min<sup>-1</sup> and 5 °C min<sup>-1</sup>, in an oxidizing atmosphere;

preparation of a slurry of the a ceramic impermeable to gaseous species, which corresponds to the electrolyte slurry (2), by ball milling, using 1 g to 4 g of the electrolyte composition, described in the present invention, using 1% to 5% of organic thickener - preferably polyvinyl polypyrrolidone - and using ethanol, which quantity ranges from 1 mL to 20 mL - preferably 6 mL; the rotation speed ranges from 100 rpm to 650 rpm, preferably between 300 rpm and 400 rpm; the effective milling time ranges from 1 h to 5 h, more preferably between 2 h and 3 h;

the electrolyte slurry (2) is subjected to an ultrasonic bath with duration ranging from 30 min to 60 min, preferably between 40 min and 50 min;

depositing layers of the electrolyte slurry (2), on the surface of the anode support (1) by spin-coating to form the electrolyte pre-layer (3); the rotation speed ranges from 500 rpm to 3000 rpm, preferably from 1500 rpm to 2000 rpm; the effective rotation time ranges from 10 s to 120 s, more preferably between 20 s and 40 s; the number of layer ranges from 1 to 5, preferably from 1 to 2 layers;

sintering of the anode / electrolyte pre-layer (3) in the temperature range 1000°C to 1300°C, preferably between 1050°C and 1150°C, for 5 h to 15 h, with an heating rate between 1°C min<sup>-1</sup> and 5°C min<sup>-1</sup>, in an oxidizing atmosphere;

depositing layers of the electrolyte slurry (2), on the surface of the electrolyte pre-layer (3) by spin-coating to form the final electrolyte layer (4); the rotation speed ranges from 500 rpm to 3000 rpm, preferably from 1500 rpm to 2000 rpm; the effective rotation time ranges from 10 s to 120 s, more preferably between 20 s and 40 s; the number of layer ranges from 1 to 5, preferably from 1 to 2 layers;

sintering of the anode / final electrolyte layer (4) in the temperature range 1300°C to 1500°C, preferably between 1350°C and 1400°C, for 5 h to 15 h, with a heating rate between 1°C min<sup>-1</sup> and 5°C min<sup>-1</sup>, in an oxidizing atmosphere. Fig. 2 depicts a top view microstructure of the anode, which is composed of both Ni (metal-fraction) and BCY (ceramic fraction) phases. Fig. 3 shows the top view microstructure of the dense electrolyte layer (4).

**[0052]** In other embodiments, the described membrane electrode assembly (MEA) can have an anode comprising a thickness, preferably, between 100µm to 1500µm, an electrolyte comprising a thickness, preferably, between 10µm to 100µm, and a cathode comprising a thickness, preferably varying from 1µm to 3000µm. This preferred configuration

allows an increased yield of ammonia.

**[0053]** The curvature of the MEA prepared by spin-coating is minimised by controlling the temperature and time during the sintering steps of anode support (1) and anode/electrolyte bilayer.

**[0054]** After obtaining the anode/electrolyte bilayer with the mentioned methods, the curvature is assessed by measuring the variation of the bilayer thickness and the angle formed between the electrolyte layer (4) and a flat surface. The control of process parameters of the spin-coating methods (suspension formulation and sintering conditions) contributes for reducing the values of curvature indicators. These values are minimized in order to increase the success rate of the following step: the cathode deposition.

**[0055]** The following embodiments describe the preparation of the cathode electrode.

In an embodiment, the application of the cathode is performed by the application of a mixture of the desired cathode composition that can be mixed manually in a mortar or mechanically in a ball mill; the number of layers applied to the cathode (5) is made in accordance with the desired thickness;

In an embodiment for better results, the cathode deposition can be performed by the wet spraying method that consists in the preparation of a suspension composed the desired composition in an alcoholic solution of PVB (polyvinylbutyral) and in its deposition on the electrolyte, using a manual aerograph, followed by a drying step;

The preparation of a slurry of the cathode (5), which corresponds to the cathode slurry (5), by ball milling, using 1 g to 4 g of the cathode composition, described in the present invention, using 1% to 5% of organic thickener - preferably polyvinyl polypyrrolidone - and using ethanol, which quantity ranges from 1 mL to 20 mL - preferably 6 mL; the rotation speed ranges from 100 rpm to 650 rpm, preferably between 300 rpm and 400 rpm; the effective milling time ranges from 1 h to 5 h, more preferably between 2 h and 3 h;

The cathode slurry (5) is subjected to an ultrasonic bath with duration ranging from 30 min to 60 min, preferably between 40 min and 50 min;

The cathode slurry (5) is deposited over the anode / final electrolyte layer (4) by spin-coating to form the final membrane electrode assembly (MEA) (6); the rotation speed ranges from 500 rpm to 3000 rpm, preferably from 1500 rpm to 2000 rpm; the effective rotation time ranges from 10 s to 120 s, more preferably between 20 s and 40 s; the number of layer ranges from 1 to 5, preferably from 1 to 2 layers;

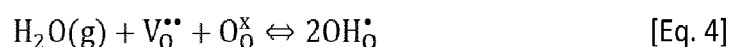
The sintering of final membrane electrode assembly (MEA) (6) in the temperature range 400°C to 1200°C, preferably between 600°C and 1150°C, for 5h to 15h, with a heating rate between 1°C min<sup>-1</sup> and 5°C min<sup>-1</sup>, in an oxidizing atmosphere. Fig. 4 depicts the cross-section view of a Fe<sub>2</sub>O<sub>3</sub>-(Na,K)OH composite cathode film. Fig. 5 shows a schematic representation of the resultant MEA, which corresponds to the MEA-SOLUTION-1.

**[0056]** In an embodiment for better results, the anode / final electrolyte layer (4) is joined to a chamber made of an electrically insulating ceramic, Al<sub>2</sub>O<sub>3</sub>, that contains the catholyte hydroxide salt mixture and metal-fraction porous layer; the metal-fraction is screen-printed on the surface of one of the Al<sub>2</sub>O<sub>3</sub> surfaces; a glass sealant is used to attach the Al<sub>2</sub>O<sub>3</sub> chamber to the electrolyte layer (4). This particular configuration benefits the rate of ammonia formation. Fig. 6 depicts the cross-section view of the MHS-PE interface, where the MSH ((Na,K)OH) became solidified after cooling down the device and wetted the BCY electrolyte surface. Fig. 7 shows a schematic representation of the resultant MEA, which corresponds to the MEA-SOLUTION-2.

Production of ammonia (NH<sub>3</sub>)

**[0057]** In an embodiment, water (steam) is used as a reagent to supply the anode side. In the presence of humidified atmospheres, proton incorporation in the PE takes place through interaction of gas-phase water molecules and oxygen-

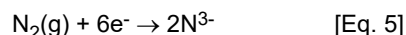
ion vacancies in the host lattice (  $V_{O}^{\bullet\bullet}$  ). In Kröger-Vink notation, the formation of protonic defects (  $OH_O^{\bullet}$  ) is given by,



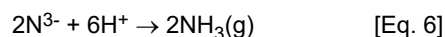
where is  $O_O^x$  an oxygen in its lattice position.

**[0058]** The protonic defects act as proton carriers (H<sup>+</sup>) that are driven through the membrane, by the application of the

electrical difference of potential, to the cathode side. At the same time, a nitrogen gas molecule is reduced to nitride ions ( $\text{N}^{3-}$ ) at the cathode metal-fraction/MHS interface, as given by,



**[0059]** The nitride ions ( $\text{N}^{3-}$ ) diffuse through the MSH, in a melt form, and then recombine with  $\text{H}^+$  diffusing from the anode side across the PE, to form ammonia, according to:



**[0060]** In addition, the applied electrical difference of potential is controlled in order to prevent the competing hydrogen evolution reaction (HER) - this can be accomplished by applying values not exceeding -1.5 V.

**[0061]** In an embodiment, nominally dry nitrogen ( $\text{N}_2$ ) is used as a reagent to supply the cathode side. The nominal absence of water prevents the occurrence of side reactions due to its interaction with formed ammonia (e.g., formation of ammonium ions,  $\text{NH}_4^+$ ). At the same time, the humidity conditions comprising a water vapor partial pressure range of  $10^{-7} \leq p_{\text{H}_2\text{O}} \leq 10^{-2}$  atm, preferably of  $10^{-6} \leq p_{\text{H}_2\text{O}} \leq 10^{-3}$  atm, more preferable of  $10^{-5} \leq p_{\text{H}_2\text{O}} \leq 10^{-4}$  atm at temperatures equal or lower than  $700^\circ\text{C}$ , preferably between  $400^\circ\text{C}$  and  $670^\circ\text{C}$ , more preferable between  $450^\circ\text{C}$  and  $550^\circ\text{C}$  are enough to ensure the absence of electronic defects that could severely hinder the electrochemical efficiency of the membrane electrode assembly (MEA), namely the yield of ammonia formation.

**[0062]** In an embodiment, in the cathode compartment, nominally dry conditions are guaranteed by the use of a gas moisture filter (Varient).

Other information

**[0063]** Furthermore, where the claims recite a composition, it is to be understood that methods of using the material for any of the purposes disclosed herein are included, and methods of making the composition according to any of the methods of making disclosed herein or other methods known in the art are included, unless otherwise indicated or unless it would be evident to one of ordinary skill in the art that a contradiction or inconsistency would arise.

**[0064]** Where ranges are given, endpoints are included. Furthermore, it is to be understood that unless otherwise indicated or otherwise evident from the context and/or the understanding of one of ordinary skill in the art, values that are expressed as ranges can assume any specific value within the stated ranges in different embodiments of the invention, to the tenth of the unit of the lower limit of the range, unless the context clearly dictates otherwise. It is also to be understood that unless otherwise indicated or otherwise evident from the context and/or the understanding of one of ordinary skill in the art, values expressed as ranges can assume any subrange within the given range, wherein the endpoints of the subrange are expressed to the same degree of accuracy as the tenth of the unit of the lower limit of the range.

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**[0066]** The term "comprising" whenever used in this document is intended to indicate the presence of stated features, integers, steps, components, but not to preclude the presence or addition of one or more other features, integers, steps, components or groups thereof.

**[0067]** The disclosure should not be seen in any way restricted to the embodiments described and a person with ordinary skill in the art will foresee many possibilities to modifications thereof. The above-described embodiments are combinable.

**[0068]** The following dependent claims further set out particular embodiments of the disclosure.

## Claims

1. A chemical/electrochemical proton ceramic membrane reactor for promote hydrogenation and de-hydrogenation reactions, in particular direct hydrogenation/de-hydrogenation of amines, at temperatures equal or lower than 700°C comprising:

a proton ceramic electrochemical cell containing a molten hydroxide catholyte and a cathode fraction;  
a ceramic protonic electrolyte membrane comprising  $A_z(B'_{1-x}B''_x)_{1-y}M_yO_{3-\delta}$

wherein A, B', B'', M are independently selected from each other;

A is selected from a list consisting of Ba<sup>2+</sup>, Sr<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, or their combination;

B' and B'' are selected from a list consisting of Zr<sup>4+</sup>, Ce<sup>4+</sup>, Sn<sup>4+</sup>, Hf<sup>4+</sup>, Mn<sup>4+</sup>, Ru<sup>4+</sup>, Pd<sup>4+</sup>, Ir<sup>4+</sup>, Pb<sup>4+</sup>, or their combination;

M is selected from a list consisting of Y<sup>3+</sup>, La<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, Dy<sup>3+</sup>, Yb<sup>3+</sup>, or their combination;

z ranges from 0.8 to 1;

x ranges from 0 to 1;

y ranges from 0 to 0.5;

δ ranges from 0 to 2.

2. The chemical/electrochemical proton ceramic membrane reactor according to the previous claim, wherein the ceramic protonic electrolyte membrane is selected from a list consisting of BaCeOs, BaZrOs, or their combinations.
3. The chemical/electrochemical proton ceramic membrane reactor according to any of the previous claims, wherein the ceramic protonic electrolyte membrane is doped, preferably doped with Sn, Gd or Y.
4. The chemical/electrochemical proton ceramic membrane reactor according to any of the previous claims, wherein M is Y<sup>3+</sup>.
5. The chemical/electrochemical proton ceramic membrane reactor according to any of the previous claims, wherein the thickness of the ceramic protonic electrolyte membrane is below 100 μm, preferably below 40 μm.
6. The chemical/electrochemical proton ceramic membrane reactor according to any of the previous claims, wherein the molten hydroxide catholyte is a binary phase of alkali-hydroxide composition  $A'_{1-x}A''_x(OH)$  catholyte

wherein A' and A'' are independently selected from each other;

A' and A'' are selected from a list consisting of Na<sup>+</sup>, K<sup>+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>;

x varies between 0 to 1.

7. The chemical/electrochemical proton ceramic membrane reactor according to any of the previous claims, wherein the binary phases of alkali-hydroxide compositions  $A'_{1-x}A''_x(OH)$  catholytes are in the form of powder, porous, or molten form, or mixtures thereof.

8. The chemical/electrochemical proton ceramic membrane reactor according to any of the previous claims, wherein the ceramic protonic electrolyte membrane operates at temperatures from 400°C to 670°C, preferably from 450°C to 550°C.

9. The chemical/electrochemical proton ceramic membrane reactor according to any of the previous claims, wherein the ceramic protonic electrolyte membrane operates at a water vapor partial pressure range from  $10^{-7}$  atm to  $10^{-2}$  atm, preferably from  $10^{-6}$  atm to  $10^{-3}$  atm, more preferably from  $10^{-5}$  atm to  $10^{-4}$  atm.

10. The chemical/electrochemical proton ceramic membrane reactor according to any of the previous claims, further comprising a composite porous anode comprising a metal-fraction and a ceramic-fraction.

11. The chemical/electrochemical proton ceramic membrane reactor according to any of the previous claims 10 to 11, wherein the porosity of the composite porous anode is below 40%, preferably between 10% and 30%, and the pore size is below 100  $\mu\text{m}$ , preferably between 10  $\mu\text{m}$  and 50  $\mu\text{m}$ .

12. The chemical/electrochemical proton ceramic membrane reactor according to any of the previous claims, wherein the cathode fraction comprises a metal-fraction and a molten hydroxide salt-fraction.

13. The chemical/electrochemical proton ceramic membrane reactor according to the previous claim 10 to 12, wherein the metal-fraction is a doped metal or metal oxide with at least one element selected from a list consisting of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, hafnium, tantalum, tungsten, iridium, platinum, gold, or mixtures thereof.

14. The chemical/electrochemical proton ceramic membrane reactor according to the previous claim, further comprising an anode chamber, preferably composed of a hydrogen-containing gas, wherein the hydrogen-containing gas is selected from a list consisting of hydrogen, nitrogen, argon, or mixtures thereof.

15. The chemical/electrochemical proton ceramic membrane reactor according to the previous claim, further comprising a cathode chamber, preferably composed of a nitrogen-containing gas, wherein the nitrogen-containing gas is selected from a list consisting of nitrogen, hydrogen, or mixtures thereof.

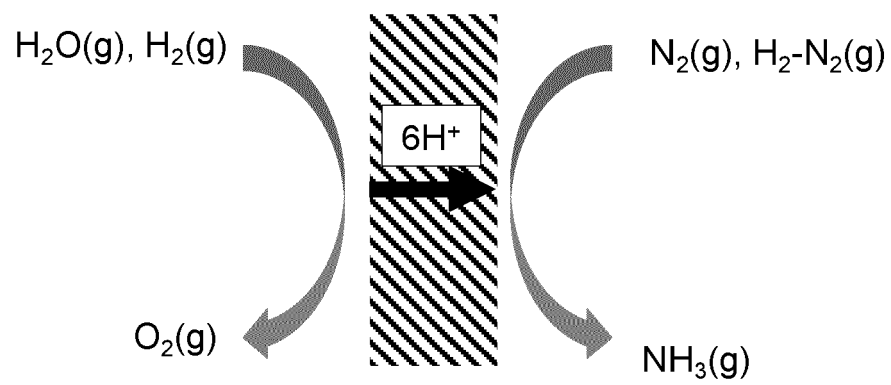


Fig. 1

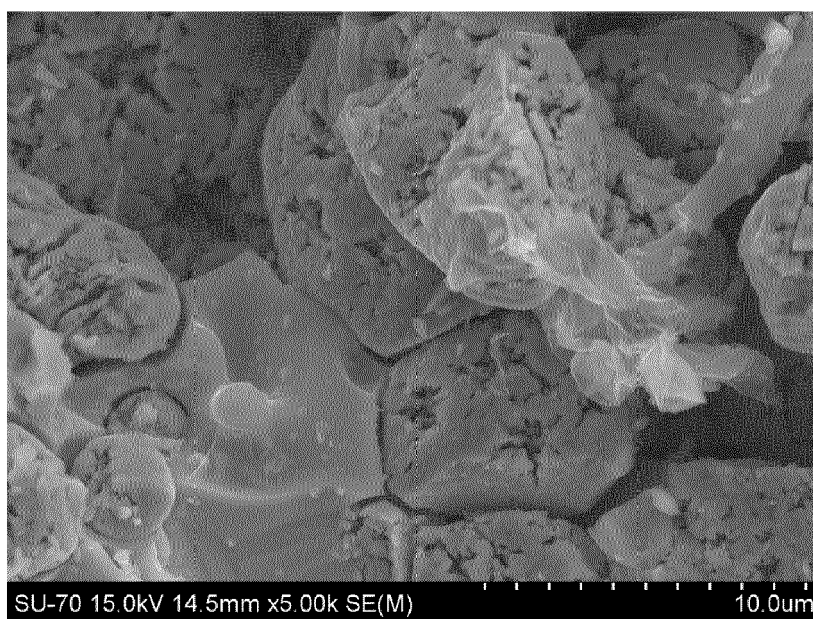


Fig. 2

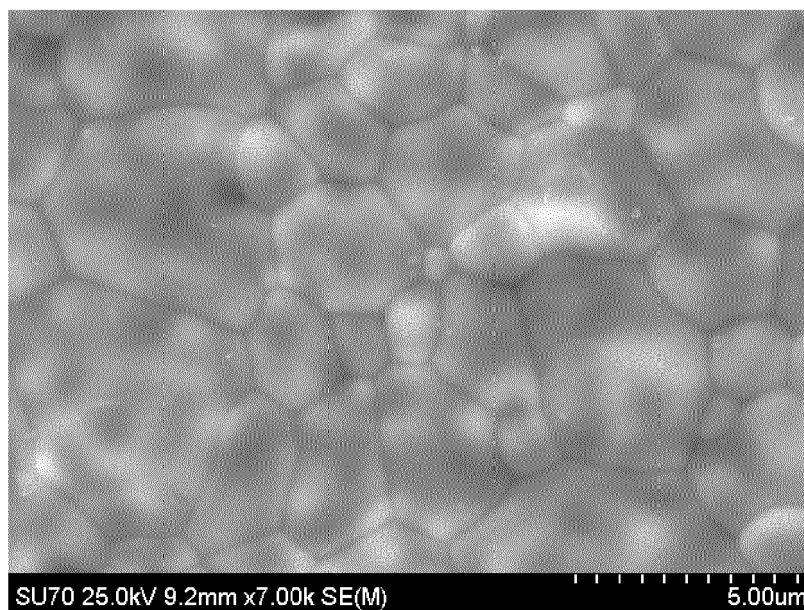


Fig. 3

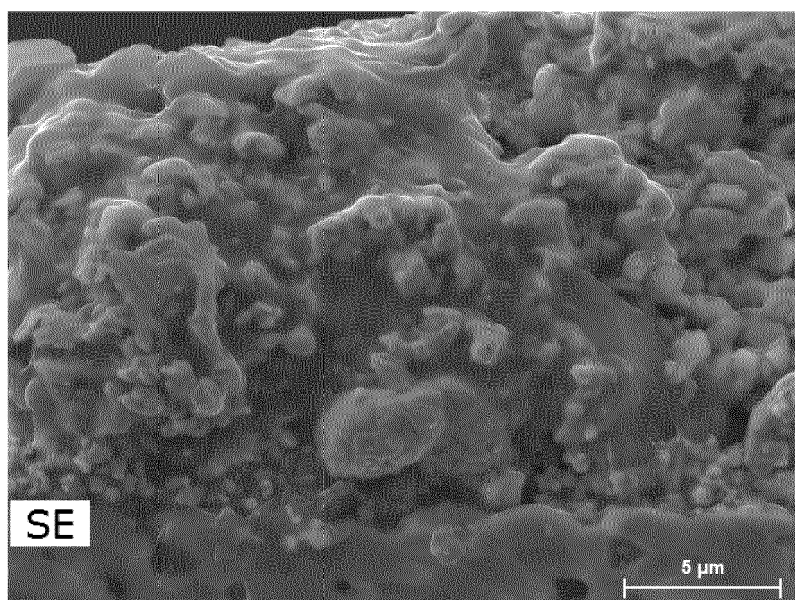


Fig. 4

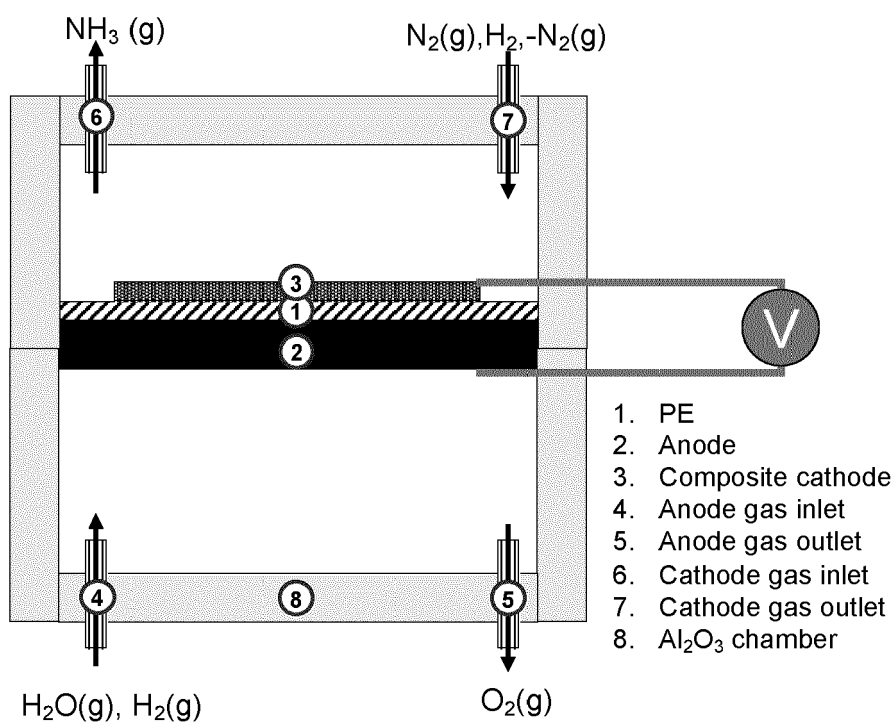


Fig. 5

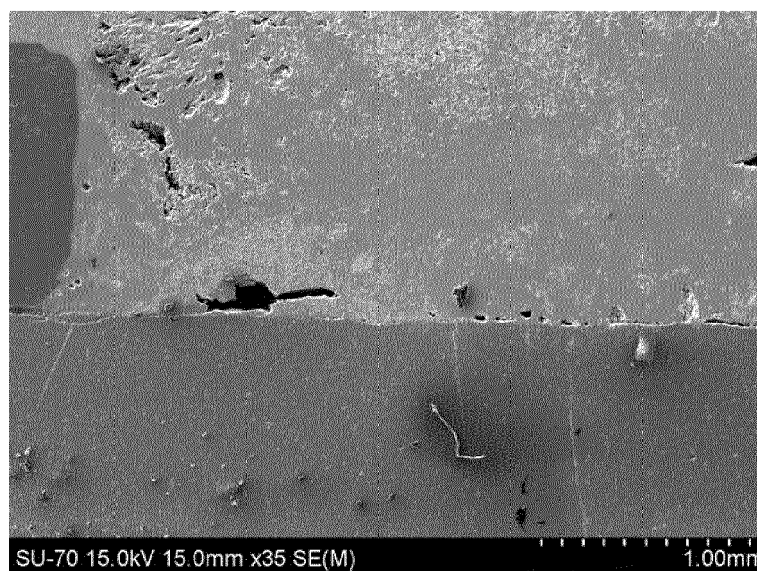


Fig. 6

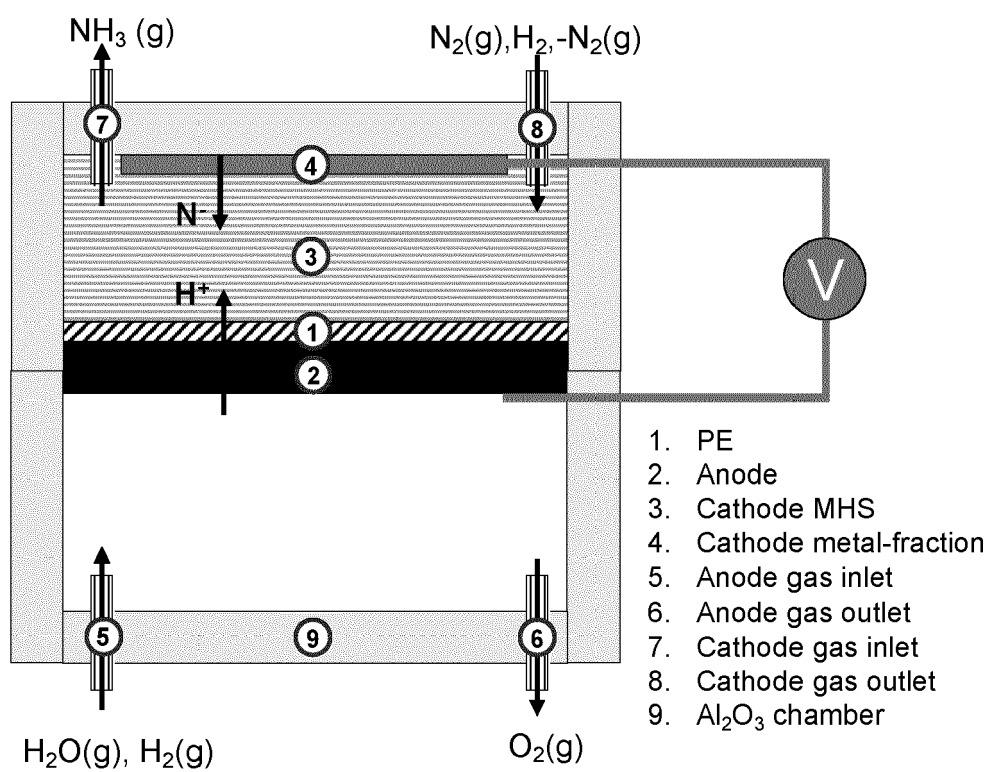


Fig. 7



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Application Number

EP 23 18 2764

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|                                                                                                                                                                                                                                                                                       |                                                                                                                                   |                                  | C25B                                                                 |
| The present search report has been drawn up for all claims                                                                                                                                                                                                                            |                                                                                                                                   |                                  |                                                                      |
| Place of search                                                                                                                                                                                                                                                                       |                                                                                                                                   | Date of completion of the search | Examiner                                                             |
| The Hague                                                                                                                                                                                                                                                                             |                                                                                                                                   | 29 November 2024                 | Helgadóttir, Inga                                                    |
| CATEGORY OF CITED DOCUMENTS                                                                                                                                                                                                                                                           |                                                                                                                                   |                                  |                                                                      |
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