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(54) Title: REACTOR COMPRISING AN EXTRACTIVE MEMBRANE, PREPARATION AND USE

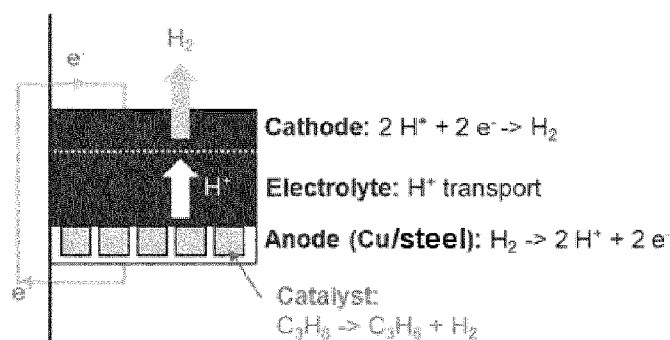


Fig. 1

(57) Abstract: The disclosure concerns a proton-conducting catalytic membrane remarkable in that it comprises an anode, an electrolyte layer disposed on top of the anode and a porous cathode disposed on top of the electrolyte layer, wherein the anode comprises at least one dehydrogenation catalyst and is devoid of pores, and wherein the electrolyte layer comprises one or more perovskite materials with one or more cations selected from Ba, Ce, Zr, Y, La, Sr, Mn, Fe, Eu, Tb, Ni, Yb, Pr, Sm, Zn, Gd, Er, Co, Nd, or any mixtures thereof. The disclosure is also about a dehydrogenation reactor comprising such proton-conducting catalytic membrane as well as to method for making such proton-conducting catalytic membrane.



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Reactor comprising an extractive membrane, preparation and use

Technical field

The present disclosure relates to a proton-conducting catalytic membrane, a dehydrogenation reactor comprising the proton-conducting catalytic membrane thereof as well as to a method
5 for making such proton-conducting catalytic membrane.

Technical background

Dehydrogenation reactions are carried out without hydrogen extraction. Thus, industrial processes are generally limited to about 50% conversion. In addition, such reactions lead to significant and fast coking of the catalyst. Industrial processes require therefore either
10 continuous decoking (with H₂ or water). H₂ produced must be separated from the product stream after the reaction.

A solution was brought by EP2534721 and/or by WO2011098525 to use a tubular reactor comprising a first zone comprising a dehydrogenation catalyst and a second zone separated from said first zone by a proton-conducting membrane comprising forming a layered structure
15 of a porous and non-porous mixed metal oxide as a support and a dehydrogenation catalyst that is deposited on the membrane and that can adhere to it or freely lie on it. Similar proton-conducting ceramic membrane are described in WO2014187978.

In US20200248321, a membrane reactor for conducting the dehydrogenation of alkanes to alkenes presents one or more tubes lined with one or more reactive ceramic membranes or
20 layered throughout the one or more tubes. The membrane reactor allows a heated feed of alkanes to come into contact with the one or more ceramic membranes, wherein an alkane would react therewith, allowing alkenes to continue to flow through the one or more tubes and out of the system in reactor effluent feed, while hydrogen generated from the reaction of the alkane with the membrane would pass through the membrane and be physically separated.

However, it appeared that the manufacturing of defect-free straight tubes is a critical issue for further development of the dense ion-conducting membrane propane-to-propylene on-purpose technology. Defects in the membrane enhance coke formation with the fatal result that the membrane was destroyed. The fragility of the membranes is also an issue.
25

Another configuration exists, in which the dehydrogenation catalyst is not in contact with the hydrogen transport membrane. Thus, WO2015052297 refers to a process for preparing
30 aromatic hydrocarbon from alkanes, wherein alkanes are contacted with a dehydrogenation

catalyst in presence of hydrogen to limit coking. The hydrogen is then extracted from the reactor with a hydrogen transport membrane made for example of mixed metal oxides.

The objective of this disclosure is therefore to provide a proton-conducting catalytic membrane that can improve the conversion of a feed-to-be-dehydrogenated.

5 Summary

The disclosure relates to a proton-conducting catalytic membrane remarkable in that it comprises an anode, an electrolyte layer disposed on top of the anode and a porous cathode disposed on top of the electrolyte layer, wherein the anode comprises at least one dehydrogenation catalyst.

10

More particularly, according to a **first aspect**, the disclosure relates to a proton-conducting catalytic membrane remarkable in that it comprises an anode, an electrolyte layer disposed on top of the anode and a porous cathode disposed on top of the electrolyte layer, wherein the anode comprises at least one dehydrogenation catalyst and is devoid of pores, and
15 wherein the electrolyte layer comprises one or more perovskite materials with one or more cations selected from Ba, Ce, Zr, Y, La, Sr, Mn, Fe, Eu, Tb, Ni, Yb, Pr, Sm, Zn, Gd, Er, Co, Nd, or any mixtures thereof.

20

Surprisingly, it was found that when one or more dehydrogenation catalysts are integrated within an anode acting as support layer of a proton-conducting catalytic membrane, and not only on the top of a proton-conducting membrane, the surface contact between the one or more dehydrogenation catalysts and the membrane is expanded and favours, therefore, the extraction of the hydrogen, displacing subsequently the chemical equilibrium towards the product during a dehydrogenation process according to Le Chatelier's principle. In addition,
25 the use of one or more perovskite materials with one or more cations selected from Ba, Ce, Zr, Y, La, Sr, Mn, Fe, Eu, Tb, Ni, Yb, Pr, Sm, Zn, Gd, Er, Co, Nd, or any mixtures thereof as the electrolyte layer favours the proton transport from the anode to the cathode.

30

This configuration leads to the improvement of the conversion of alkane into alkene, for example of the conversion of propane into propene.

35

With preference, the anode comprises one or more channels, each of said channels comprising the one or more dehydrogenation catalysts. For example, the anode comprises one or more channels arranged in parallel to each other, each of said channels comprising the one or more dehydrogenation catalysts. For example, at least a part of said one or more

channels are rectangular channels, flared depth channels, flared width channels, bended channels, or corrugated channels; more preferably, all of said one or more channels are rectangular channels or flared depth channels; even more preferably, all of said one or more channels are flared depth channels.

5

With preference, the anode comprises one or more channels, each of said channels comprising the one or more dehydrogenation catalysts; wherein said one or more channels are rectangular channels or flared depth channels; and are made in copper or steel.

10 More preferably, the anode comprises one or more channels, each of said channels comprising the one or more dehydrogenation catalysts; wherein said one or more channels are flared depth channels; and are made in copper or steel.

15 Advantageously, the proton-conducting catalytic membrane presents a hydrogen extraction ratio ranging between 0.20 and 0.99, or between 0.25 and 0.90, at a temperature of at least 500°C and/or at a pressure of at most 0.1 MPa, the hydrogen extraction ratio being simulated by computational fluid dynamics (CFD) and/or quantified by gas chromatography (GC) during the reaction; with preference, the proton-conducting catalytic membrane presents a hydrogen
20 extraction ratio ranging between 0.20 and 0.99, or between 0.25 and 0.90, at a temperature of at least 550°C and/or at a pressure of at most 0.05 MPa.

Advantageously, the anode is made of one or more first metals and/or of one or more spinels. With preference, the one or more first metals are selected from Cu, Fe, Cr, Ag, Ni, Mo, Pt, Pd, Au, Mn or any mixtures thereof, more preferably from Cu, Fe, Cr, Ag, Ni, Mo, Pt, Pd or any
25 mixtures thereof; even more preferably from Cu, Fe, Cr, Ag, Ni, Mo, or any mixtures thereof, most preferably from Cu, Fe, Cr, Ag, Ni or any mixtures thereof, such as Cu, Fe, Cr, Ni or any mixtures thereof, or such as Cu, Fe, Cr or any mixtures thereof, or such as Cu and/or Ag. For example, the one or more first metals and/or the one or more spinels are doped with one or
30 more dopants, preferably selected from Cu, Li, Cr or a mixture thereof.

Advantageously, the anode is made of or comprises steel.

For example, the anode is made of or comprises stainless steel, more preferably ferritic
35 stainless steel.

For example, the steel comprises between 60 wt.% and 80 wt.% of iron based on the total weight of the steel, preferably between 63 wt.% and 75 wt.% of iron.

5 For example, the steel comprises between 11 wt.% and 18 wt.% of chromium based on the total weight of the steel, preferably between 12 wt.% and 17 wt.%.

For example, the steel comprises between 10 wt.% and 14 wt.% of nickel based on the total weight of the steel, preferably between 11 wt.% and 13 wt.%.

10 For example, the steel comprises between 1 wt.% and 3 wt.% of molybdenum.

For example, the steel comprises less than 0.15 wt.% of carbon based on the total weight of the steel, preferably less than 0.12 wt.%.

15 For example, the steel comprises at least 60 wt.% of iron and between 11 wt.% and 18 wt.% of chromium based on the total weight of the steel. With preference, the steel also comprises less than 0.15 wt.% of carbon based on the total weight of steel; preferably less than 0.12 wt.%.

20 For example, the steel comprises between 60 wt.% and 80 wt.% of iron, between 11 wt.% and 18 wt.% of chromium and less than 0.15 wt.% of carbon, based on the total weight of the steel.

For example, the anode is devoid of pores.

25 Advantageously, the one or more dehydrogenation catalysts comprise one or more metal-based catalysts, one or more metal oxide-based catalysts, one or more zeolites, one or more transition metal carbides, one or more transition metal nitrides, one or more carbon nanotubes, or any mixtures thereof. With preference, the one or more dehydrogenation catalysts comprise one or more metal-based catalysts, one or more metal oxide-based catalysts, one or more
30 zeolites, or any mixtures thereof. More preferably, the one or more dehydrogenation catalysts comprise one or more metal-based catalysts. For example, the one or more zeolites are selected from the group of CHA, MFI families or any mixtures thereof. For example, the one or more zeolites are doped with one or metals selected from Mo, W, Fe, V, Cr or any mixtures thereof. For example, the one or more metal-based catalysts and/or the one or more metal
35 oxide-based catalyst comprises one or more metals selected from Pd, Pt, Sn, Mo, W, Fe, V, Cr or any mixtures thereof.

Advantageously, the electrolyte of the electrolyte layer is or comprises one or more perovskite materials with one or more cations selected from Ba, Ce, Zr, Y, La, Sr, Mn, Fe, Eu, Tb, Ni, Yb, Pr, Sm, Zn, Gd, Er, Co, Nd, or any mixtures thereof; with preference, said one or more cations are selected from Ba, Ce, Zr, Y, Ni, or any mixtures thereof; more preferably, said one or more cations are selected from Ba, Ce, Zr, Y, or any mixtures thereof.

Advantageously, the electrolyte of the electrolyte layer is or comprises one or more perovskite materials with an electrical conductivity ranging between 10^{-4} S/cm and 10^{-3} S/cm as determined by electrochemical impedance spectroscopy measurements performed at 600°C under an atmosphere comprising Ar and H₂ in a ratio 75/25.

Advantageously, the anode has a thickness ranging between 3 mm and 6 mm as designed by SolidWorks software, preferably between 3.5 mm and 5.5 mm.

Advantageously, the electrolyte layer has a thickness ranging between 20 µm and 40 µm as determined by scanning electron microscopy, preferably between 25 µm and 35 µm.

Advantageously, the porous cathode has a thickness ranging between 30 µm and 50 µm as determined by scanning electron microscopy, preferably between 35 µm and 45 µm.

Advantageously, the porous cathode comprises a mixture of one or more electrolytes and one or more second metals. For example, the one or more second metals are selected from Ni, Fe, Co, Pd, Pt, or any mixtures thereof, more preferably Ni. With preference, the amount of the one or more second metals is ranging between 50 wt.% and 70 wt.% of the total weight of said mixture, more preferably between 55 wt.% and 65 wt.%. For example, the amount of nickel is ranging between 50 wt.% and 70 wt.% of the total weight of said mixture, more preferably between 55 wt.% and 65 wt.%.

For example, the porous cathode is a macroporous layer.

Advantageously, the proton-conducting catalytic membrane is a co-ionic catalytic membrane.

According to a **second aspect**, the disclosure relates to a dehydrogenation reactor, remarkable in that it comprises at least one proton-conducting catalytic membrane as defined in accordance with the first aspect.

With preference, the dehydrogenation reactor has a planar geometry. It has been indeed noticed that when the reactor module is designed to reduce gas polarization, by being planar, it is still possible to improve the extracting capability of the proton-conducting catalytic membrane that is described above. Such dehydrogenation reactor further minimizes coking formation and therefore preserves the activity of the one or more dehydrogenation catalysts.

In an embodiment, the dehydrogenation reactor comprises an arrangement of at least two proton-conducting catalytic membranes arranged on top of each other, preferably an arrangement of at least three, or of at least four, or of at least five.

In another complementary and/or alternative embodiment, the dehydrogenation reactor comprises an arrangement of at least two proton-conducting catalytic membranes which are coplanar with each other and/or adjacent with each other.

Advantageously, whichever the embodiment selected or when said dehydrogenation reactor comprises more than one proton-conducting catalytic membrane, said dehydrogenation reactor further comprises a spacer between each proton-conducting membrane. For example, the spacer is an electro-conducting plate, preferably a steel plate, more preferably a stainless steel plate, even more preferably a ferritic stainless steel plate.

Advantageously, said reactor has an inlet and an outlet, and said reactor is remarkable in that the inlet is in a first zone arranged so that a feed to said reactor via the inlet contacts the one or more dehydrogenation catalysts of the proton-conducting catalytic membrane before passing to the outlet, the outlet being for example in a second zone that is downstream of the proton-conducting catalytic membrane. With preference, the inlet has surface area identical to the surface area of the outlet or the inlet has a surface area smaller than the surface area of the outlet. More preferably, the inlet has a surface area smaller than the surface area of the outlet.

Advantageously, said reactor has an inlet and an outlet, and said reactor is remarkable in that the anode of the one or more proton-conducting catalytic membranes comprises one or more channels, each of said channels comprising the one or more dehydrogenation catalysts, and in that the inlet is in a first zone arranged so that a feed to said reactor via the inlet is conducted through the one or more channels and contacts the one or more dehydrogenation catalysts before passing to the outlet being for example in a second zone that is downstream of the proton-conducting catalytic membrane. With preference, the inlet has surface area identical to the surface area of the outlet or the inlet has a surface area smaller than the surface area of

the outlet. More preferably, the inlet has a surface area smaller than the surface area of the outlet.

Advantageously, said reactor has an inlet and an outlet, and said reactor is remarkable in that the surface area of the outlet is at least 2 times larger than the surface area of the inlet, more preferably at least 2.5 times, even more preferably at least 2.75 times, most preferably at least 3 times.

With preference, the inlet and outlet of the reactor are arranged on faces of the reactor that are opposed to each other. In other words, the inlet is in a first zone arranged so that a feed to said reactor via the inlet is conducted towards the proton-conducting catalytic membrane and the outlet is in a second zone that is downstream of the proton-conducting catalytic membrane. With preference, the first zone and the second zone each form one face of the reactor and are advantageously opposed to each other. Alternatively, the first zone and the second zone are arranged on a single face of the reactor.

According to a **third aspect**, the disclosure relates to a method for making a **proton-conducting membrane**, remarkable in that said method comprises the following steps:

- a) providing a mixture of one or more electrolytes and one or more second metals to form a solution of mixed oxides;
- b) pressing uniaxially the mixture provided at step (a) to form a porous cathode;
- c) optionally, calcining said porous cathode
- d) providing one or more electrolytes;
- e) screen-printing said one or more electrolytes on the porous cathode or on the calcined porous cathode if step (c) is carried out, to obtain a porous cathode with an electrolyte layer;
- f) sintering said porous cathode with an electrolyte layer, to obtain a sintered porous cathode with an electrolyte layer;
- g) providing an anode made of one or more first metals and/or of one or more spinels;
- i) coating said anode provided at step (g) on the electrolyte layer of the sintered porous cathode obtained at step (f), so as to obtain a proton-conducting membrane.

According to a **fourth aspect**, the disclosure relates to a method for making a proton-conducting catalytic membrane as defined according to the first aspect, remarkable in that said method comprises a method for making a proton-conducting membrane as defined in the

third aspect, and in that the method for making a proton-conducting membrane as defined in the third aspect further comprises after the step (g), the step (h) of depositing at least one dehydrogenation catalyst on said anode provided at step (g), so as to form a catalytic anode, and wherein the step (i) is the step of assembling together the sintered porous cathode with an electrolyte layer of step (f) with the catalytic anode formed at step (h), preferably by sealing with one or more sealants, so as to obtain a proton-conducting catalytic membrane as defined according to the first aspect.

In other words, according to the fourth aspect, the disclosure relates to a method for making a proton-conducting catalytic membrane as defined according to the first aspect, remarkable in that said method comprises the following steps:

- a) providing a mixture of one or more electrolytes and one or more second metals to form a solution of mixed oxides;
- b) pressing uniaxially the mixture provided at step (a) to form a porous cathode;
- c) optionally, calcining said porous cathode
- d) providing one or more electrolytes;
- e) screen-printing said one or more electrolytes on the porous cathode or on the calcined porous cathode if step (c) is carried out, to obtain a porous cathode with an electrolyte layer;
- f) sintering said porous cathode with an electrolyte layer;
- g) providing an anode made of one or more first metals and/or of one or more spinels;
- h) depositing at least one dehydrogenation catalyst on said anode provided at step (g), so as to form a catalytic anode;
- i) assembling together the sintered porous cathode with an electrolyte layer of step (f) with the catalytic anode formed at step (h), so as to obtain a proton-conducting catalytic membrane as defined according to the first aspect.

One or more of the following features advantageously further define the third and/or the fourth aspect:

- Before step (a), an activation step is carried out under activation conditions on the oxidized form of the one or more second metals. For example, the activation conditions comprise providing a reduction atmosphere comprising preferably between 15 vol.% and 50 vol.% of hydrogen and between 85 vol.% and 50 vol.% of an inert gas based on the total volume of the reduction atmosphere. For example, the inert gas is Ar, He, N₂ or a mixture thereof, preferably Ar. For example, the activation conditions comprise a temperature ranging between 600°C and 800°C, preferably between 650°C and 750°C. For example, the activation conditions comprise a reduction time ranging

between 5 hours and 15 hours, preferably between 7 hours and 13 hours. With preference, a calcination step is carried out before said activation step, preferably at a temperature ranging between 600°C and 800°C, more preferably between 650°C and 750°C. For example, the calcination step is carried out under an inert gas atmosphere, such as under Ar, He, N₂ or a mixture thereof, preferably under Ar.

- The one or more electrolytes provided at step (a) is a solid solution of at least two perovskite materials.
- The mixture of step (a) further comprises one or more polar aprotic solvents, such as one or more of acetone, dimethyl formamide, dimethyl sulfoxide, or a mixture thereof, preferably acetone.
- The mixture provided at step (a) further comprises one or more polymers selected from polyvinyl alcohol (PVA) or poly(methyl methacrylate) (PMMA), preferably polyvinyl alcohol (PVA). For example, the mixture provided at step (a) comprises said one or more polymers and mixed oxides at a ratio ranging between 1/0.050 and 1/0.100, preferably between 1/0.060 and 1/0.090, more preferably between 1/0.070 and 1/0.080.
- Step (a) is performed by grinding the mixture of one or more electrolytes and one or more second metals, preferably for at least 12 hours, more preferably for a time ranging between 18 hours and 36 hours, even more preferably ranging between 20 hours and 32 hours.
- After step (a) and before step (b), a drying step is performed. For example, the drying step is performed at a temperature ranging between 40°C and 80°C, preferably between 50°C and 70°C.
- The one or more first metals are selected from Cu, Fe, Cr, Ag, Ni, Mo, Pt, Pd, Au, Mn or any mixtures thereof, more preferably from Cu, Fe, Cr, Ag, Ni, Mo, Pt, Pd or any mixtures thereof; even more preferably from Cu, Fe, Cr, Ag, Ni, Mo, or any mixtures thereof, most preferably from Cu, Fe, Cr, Ag, Ni or any mixtures thereof, such as Cu, Fe, Cr, Ni or any mixtures thereof, or such as Cu, Fe, Cr or any mixtures thereof, or such as Cu and/or Ag.
- The one or more second metals are selected from Ni, Fe, Co, Pd, Pt, or any mixtures thereof, more preferably Ni.
- The one or more first metals and/or the one or more spinels are doped with one or more dopants, preferably selected from Cu, Li, Cr or a mixture thereof.
- Step (b) is the step of pressing uniaxially at a force ranging between 30 kN and 50 kN, preferably between 35 kN and 45 kN.
- When step (c) is carried out, said step (c) is performed at a temperature ranging between 600°C and 800°C, preferably between 650°C and 750°C.

- When step (c) is carried out, step (c) is performed during a time ranging between 5 hours and 15 hours, preferably between 7 hours and 13 hours.
- The one or more electrolytes provided at step (a) and/or at step (d) are or comprise one or more perovskite materials with one or more cations selected from Ba, Ce, Zr, Y, La, Sr, Mn, Fe, Eu, Tb, Ni, Yb, Pr, Sm, Zn, Gd, Er, Co, Nd, or any mixtures thereof; with preference, said one or more cations are selected from Ba, Ce, Zr, Y, Ni or any mixture thereof; more preferably, said one or more cations are selected from Ba, Ce, Zr, Y, or any mixtures thereof.
- The one or more electrolytes provided at step (a) and/or at step (d) are or comprise one or more perovskite materials with an electrical conductivity ranging between 10^{-4} S/cm and 10^{-3} S/cm as determined by electrochemical impedance spectroscopy measurements performed at 600°C under an atmosphere comprising Ar and H₂ in a ratio 75/25.
- The one or more electrolytes provided at step (d) are the same as the one or more electrolytes provided in the mixture with one or more second metals.
- Step (f) is performed at a temperature ranging between 1300°C and 1700°C, preferably between 1350°C and 1650°C, more preferably between 1400°C and 1600°C.
- Step (f) is performed for a time of at least 5 hours, preferably during 10 hours and 15 hours.
- Before step (h) a step of forming one or more channels within the anode provided at step (g) is carried out. With preference, said step of forming one or more channels is performed by electroforming or electroplating the anode provided at step (g). For example, said step of forming one or more channels is performed by chemical vapour deposition (CVD), physical vapour deposition (PVD), thermal spraying, microfabrication by etching, photolithography, tri-dimensional printing (such as fused deposition modelling, stereolithography or selective laser sintering), machining (such as milling, drilling or stamping), or any combination thereof.
- Before step (i), a step of covering the electrochemical cell of step (f) with a layer of the same one or more first metals as those making the anode provided at step (g) is carried out.
- The step (i) is performed by sealing together the electrochemical cell of step (f) with the catalytic anode formed at step (h) with one or more sealants. For example, the one or more sealants are one or more sealing tapes and/or one or more sealing pastes, more preferably one or more sealing tapes.

According to a **fifth aspect**, the disclosure relates to a method for preparing a dehydrogenation reactor as defined in accordance with the second aspect, remarkable in that said method comprises the following steps:

- a) providing a reactor, preferably a reactor with a planar geometry;
- 5 b) inserting the proton-conducting catalytic membrane as defined according to the first aspect within said reactor and/or as produced according to the method of the fourth aspect.

10 According to a **sixth aspect**, the disclosure relates to an use of a proton-conducting catalytic membrane as defined in accordance with the first aspect and/or of a dehydrogenation reactor as defined in accordance with the second aspect in a dehydrogenation reaction.

For example, the dehydrogenation reaction is a propane dehydrogenation reaction and/or an ethane dehydrogenation, more preferably a propane dehydrogenation reaction.

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Description of the figures

- Figure 1: Scheme of the three layers forming the proton-conducting catalytic membrane of the present disclosure.
- Figure 2: Scanning electron microscopy image of the proton-conducting catalytic
20 membrane of the present disclosure.
- Figure 3: Scheme of a propane dehydrogenation (PDH) process carried out with the proton-conducting catalytic membrane of the present disclosure.
- Figure 4: Scheme of a rectangular channel arranged in the anode of a dehydrogenation reactor of the present disclosure.
- 25 - Figure 5: Scheme of a flared depth channel arranged in the anode of a dehydrogenation reactor of the present disclosure, the flared depth channel having a surface area of the outlet larger than the surface area of the inlet.
- Figure 6: Representation of the mechanism when a co-ionic catalytic membrane is used.
- 30 - Figure 7: Arrangement of 4 proton-conducting catalytic membranes according to the present disclosure in a stacking forming a dehydrogenation reaction with 4 membranes working in parallel.
- Figure 8: Arrangement of 20 proton-conducting catalytic membranes according to the present disclosure in a stacking forming a dehydrogenation reaction with 20
35 membranes working in parallel.

- Figure 9: Electrochemical Impedance Spectroscopy (EIS) measurements of the electrolyte used in the present disclosure. Z' and Z'' are respectively the real and the imaginary part of the impedance, each part corresponding to the two phases of the electrical impedance. The real part corresponds to the resistance R while the imaginary part corresponds to the reactance X .
- Figure 10: Zoom-in of figure 9 at the zone of the intersect of the curves with the abscissa.
- Figure 11: Conductivity measurement of the electrolytes used in the present disclosure. The electrolytes **1A** and **1B** have been pre-calcined and then sintered at 700 °C while the electrolyte **2A** has been sintered at 700°C.
- Figure 12: Evolution of the electrical potential in function of the area specific resistance in the proton-conducting catalytic membrane according to the disclosure.
- Figure 13: Conversion of propane into propene in function of the H_2 extraction ratio with respect to the temperature.
- Figure 14: Conversion of propane into propene in function of the H_2 extraction ratio with respect to the pressure.
- Figure 15: Propane conversion and propylene selectivity at a space velocity of 150 Nml/h/g as a function of the temperature and the hydrogen extraction ratio.
- Figure 16: Propane conversion and propylene selectivity at a space velocity of 750 Nml/h/g as a function of the temperature and the hydrogen extraction ratio.
- Figure 17: Simulation by computational fluid dynamics (CFD) of the coke formation in function of the temperature within the proton-conducting catalytic membranes of the present disclosure.
- Figure 18: Representation of a flared depth channel in accordance with the present disclosure.
- Figure 19: Evolution of the amount of coke in function of the reactor length in the absence of steam in the flared depth channel of figure 18.
- Figure 20: Evolution of the amount of coke in function of the reactor length when water is co-fed with the propane and when the reactor employs a proton-conducting catalytic membrane in accordance with the disclosure in the flared depth channel of figure 18.
- Figure 21: Evolution of the amount of coke in function of the reactor length when water is co-fed with the propane and when the reactor employs a co-ionic catalytic membrane in accordance with the disclosure in the flared depth channel of figure 18.
- Figure 22: Propylene yield as a function of the time on stream (TOS) comprising water at a molar fraction of 2.7 %.
- Figure 23: Propylene yield as a function of the time on stream (TOS) comprising water at a molar fraction of 5.4 %.

- Figure 24: Propylene yield as a function of the time on stream (TOS) comprising water at a molar fraction of 7.9 %.
- Figure 25: Proton-conducting catalytic membrane in which the anode is made of copper, the membrane being incorporated within a steel housing.
- 5 - Figure 26: Proton-conducting catalytic membrane in which the anode is made of stainless steel.
- Figure 27: Photograph of the proton-conducting catalytic membrane in which the anode is made of stainless steel.

Detailed description

- 10 For the disclosure, the following definitions are given:

The terms "comprising", "comprises" and "comprised of" as used herein are synonymous with "including", "includes" or "containing", "contains", and are inclusive or open-ended and do not exclude additional, non-recited members, elements or method steps. The terms "comprising", "comprises" and "comprised of" also include the term "consisting of".

- 15 The recitation of numerical ranges by endpoints includes all integer numbers and, where appropriate, fractions subsumed within that range (e.g., 1 to 5 can include 1, 2, 3, 4, 5 when referring to, for example, a number of elements, and can also include 1.5, 2, 2.75 and 3.80, when referring to, for example, measurements). The recitation of endpoints also includes the recited endpoint values themselves (e.g., from 1.0 to 5.0 includes both 1.0 and 5.0). Any
- 20 numerical range recited herein is intended to include all sub-ranges subsumed therein.

The space velocity (Nml/h/g) is measured in term of the volumetric flow rate (Nml/h) of the reactant at 0°C and 1.01 bar per gram of catalyst (g⁻¹). The volumetric flow rate of a fluid is expressed in Nml/h ("N" stands for "Normalized"), which corresponds to 1 cm³_{NTP}/h.

- 25 The feed flow (T/h) is measured by a flowmeter and corresponds to the amount of ton per hour that is flowing.

The particular features, structures, characteristics or embodiments may be combined in any suitable manner, as would be apparent to a person skilled in the art from this disclosure, in one or more embodiments.

- 30 The present disclosure relates to a proton-conducting catalytic membrane remarkable in that it comprises an anode, an electrolyte layer disposed on top of the anode and a porous cathode disposed on top of the electrolyte layer, and wherein the anode is an anode which comprises

at least one dehydrogenation catalyst. The proton-conducting catalytic membrane of the present disclosure act as an extractive membrane that removes the hydrogen that is produced during a dehydrogenation process. In particular, the present disclosure relates to a proton-conducting membrane remarkable in that it comprise an anode, an electrolyte layer disposed on top of the anode and a porous cathode disposed on top of the electrolyte layer, wherein the anode comprises at least one dehydrogenation catalyst and is devoid of pores, and wherein the electrolyte layer comprises one or more perovskite materials with one or more cations selected from Ba, Ce, Zr, Y, La, Sr, Mn, Fe, Eu, Tb, Ni, Yb, Pr, Sm, Zn, Gd, Er, Co, Nd, or any mixtures thereof. It is schematized in figures 1 and 3, and imaged by scanning electron microscopy in figure 2.

A method for making the proton-conducting catalytic membrane is also described. The method comprises the following steps:

- a) providing a mixture of one or more electrolytes and one or more second metals to form a solution of mixed oxides;
- b) pressing uniaxially the mixture provided at step (a) to form a porous cathode, for example at a force ranging between 30 kN and 50 kN, preferably between 35 kN and 45 kN;
- c) optionally, calcining said porous cathode
- d) providing one or more electrolytes;
- e) screen-printing said one or more electrolytes on the porous cathode or on the calcined porous cathode if step (c) is carried out, to obtain a porous cathode with an electrolyte layer;
- f) sintering said porous cathode with an electrolyte layer, to obtain a sintered porous cathode with an electrolyte layer;
- g) providing an anode made of one or more first metals and/or one or more spinels;
- h) depositing at least one dehydrogenation catalyst on said anode provided at step (g), so as to form a catalytic anode;
- i) assembling together the sintered porous cathode with an electrolyte layer of step (f) with the catalytic anode formed at step (h), preferably by sealing with one or more sealants, so as to obtain a proton-conducting catalytic membrane as defined according to the first aspect.

The screen-printing technology, used at step (e), is a printing technique where a mesh, for example a 21 mesh, is used to transfer an ink onto a substrate. In this case, the substrate is a porous cathode and the ink is made essentially of the electrolyte.

The steps (a) to (f) are the steps for preparing a sintered porous cathode with an electrolyte layer of a proton-conducting membrane or of a proton-conducting catalytic membrane.

Before step (a), an activation step can be carried out under activation conditions on the oxidized form of the one or more second metals. For example, the activation conditions comprise providing a reduction atmosphere comprising preferably between 15 vol.% and 50 vol.% of hydrogen and between 85 vol.% and 50 vol.% of an inert gas based on the total volume of the reduction atmosphere. For example, the inert gas is Ar, He, N₂ or a mixture thereof, preferably Ar. For example, the activation conditions comprise a temperature ranging between 600°C and 800°C, preferably between 650°C and 750°C. For example, the activation conditions comprise a reduction time ranging between 5 hours and 15 hours, preferably between 7 hours and 13 hours. With preference, a calcination step is carried out before said activation step, preferably at a temperature ranging between 600°C and 800°C, more preferably between 650°C and 750°C. For example, the calcination step is carried out under an inert gas atmosphere, such as under Ar, He, N₂ or a mixture thereof, preferably under Ar.

The one or more electrolytes provided at step (a) can be a solid solution of at least two perovskite materials. The mixture of step (a) can further comprise one or more polar aprotic solvents, such as one or more of acetone, dimethyl formamide, dimethyl sulfoxide, or a mixture thereof, preferably acetone.

The mixture provided at step (a) can further comprise, to favour the pressing, one or more polymers selected from polyvinyl alcohol (PVA) or poly(methyl methacrylate) (PMMA), preferably polyvinyl alcohol (PVA). For example, the mixture provided at step (a) comprises said one or more polymers and mixed oxides at a ratio ranging between 1/0.050 and 1/0.100, preferably between 1/0.060 and 1/0.090, more preferably between 1/0.070 and 1/0.080.

Step (a) can be performed by grinding the mixture of one or more electrolytes and one or more second metals, preferably for at least 12 hours, more preferably for a time ranging between 18 hours and 36 hours, even more preferably ranging between 20 hours and 32 hours.

After step (a) and before step (b), a drying step can be performed. For example, the drying step is performed at a temperature ranging between 40°C and 80°C, preferably between 50°C and 70°C.

The one or more first metals are advantageously selected from Cu, Fe, Cr, Ag, Ni, Mo, Pt, Pd, Au, Mn or any mixtures thereof, more preferably from Cu, Fe, Cr, Ag, Ni, Mo, Pt, Pd or any

mixtures thereof; even more preferably from Cu, Fe, Cr, Ag, Ni, Mo, or any mixtures thereof, most preferably from Cu, Fe, Cr, Ag, Ni or any mixtures thereof, such as Cu, Fe, Cr, Ni or any mixtures thereof, or such as Cu, Fe, Cr or any mixtures thereof, or such as Cu and/or Ag. The one or more first metals and/or the one or more spinels can be doped with one or more
5 dopants, preferably selected from Cu, Li, Cr or a mixture thereof.

The one or more second metals are advantageously selected from Ni, Fe, Co, Pd, Pt, or any mixtures thereof, more preferably Ni.

10 When step (c) is carried out, said step (c) can be performed at a temperature ranging between 600°C and 800°C, preferably between 650°C and 750°C; and/or during a time ranging between 5 hours and 15 hours, preferably between 7 hours and 13 hours.

The one or more electrolytes provided at step (a) and/or at step (d) can be or comprise one or
15 more perovskite materials with one or more cations selected from Ba, Ce, Zr, Y, La, Sr, Mn, Fe, Eu, Tb, Ni, Yb, Pr, Sm, Zn, Gd, Er, Co, Nd, or any mixtures thereof; with preference, said one or more cations are selected from Ba, Ce, Zr, Y, Ni, or any mixtures thereof; more preferably, said one or more cations are selected from Ba, Ce, Zr, Y, or any mixtures thereof. For example, they are or comprise one or more perovskite materials with an electrical
20 conductivity ranging between 10^{-4} S/cm and 10^{-3} S/cm as determined by electrochemical impedance spectroscopy measurements performed at 600°C under an atmosphere comprising Ar and H₂ in a ratio 75/25. Advantageously, the one or more electrolytes provided at step (d) are the same as the one or more electrolytes provided in the mixture with one or more second metals.

25

The step (f) of sintering is the process of compacting and forming a solid mass by pressure and/or heat without melting the solid mass to its point of liquefaction. Step (f) can be performed at a temperature ranging between 1300°C and 1700°C, preferably between 1350°C and 1650°C, more preferably between 1400°C and 1600°C. Step (f) can be performed for a time
30 of at least 5 hours, preferably during 10 hours and 15 hours.

The steps (g) and (i) are the steps of making an anode on the electrolyte layer of the sintered porous cathode, the anode comprising ideally one or more dehydrogenation catalysts provided at step (h) so that the proton-conducting membrane is a proton-conducting catalytic
35 membrane and can be used for example in a dehydrogenation process.

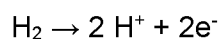
Before step (h) a step of forming one or more channels within the anode provided at step (g) can be carried out. With preference, said step of forming one or more channels is performed by electroforming or electroplating the anode provided at step (g). For example, said step of forming one or more channels is performed by chemical vapour deposition (CVD), physical vapour deposition (PVD), thermal spraying, microfabrication by etching, photolithography, tri-dimensional printing (such as fused deposition modelling, stereolithography or selective laser sintering), machining (such as milling, drilling or stamping), or any combination thereof.

Before step (i), a step of covering the electrochemical cell of step (f) with a layer of the same one or more first metals as those making the anode provided at step (g) can be carried out. The step (i) is advantageously performed by sealing together the electrochemical cell of step (f) with the catalytic anode formed at step (h) with one or more sealants. For example, the one or more sealants are one or more sealing tapes and/or one or more sealing pastes, more preferably one or more sealing tapes.

The anode

The anode is an electroconductive layer. The anode comprises at least one dehydrogenation catalyst and is devoid of pores.

For example, the anode is made of one or more first metals, and/or of one or more spinels (*i.e.*, MgAl_2O_4). This is an electroconductive layer, where hydrogen is transformed into protons (H^+), following the chemical equation (1):



With preference, the one or more first metals are selected from from Cu, Fe, Cr, Ag, Ni, Mo, Pt, Pd, Au, Mn or any mixtures thereof, more preferably from Cu, Fe, Cr, Ag, Ni, Mo, Pt, Pd or any mixtures thereof; even more preferably from Cu, Fe, Cr, Ag, Ni, Mo, or any mixtures thereof, most preferably from Cu, Fe, Cr, Ag, Ni or any mixtures thereof, such as Cu, Fe, Cr, Ni or any mixtures thereof, or such as Cu, Fe, Cr or any mixtures thereof, or such as Cu and/or Ag. Silver is the highest conducting metals while copper is the cheapest. The one or more first metals and/or the one or more spinels can be preferably doped with one or more dopants which can be selected from Cu, Li, Cr or a mixture thereof.

Advantageously, the anode is made of or comprises steel.

For example, the anode is made of or comprises stainless steel, more preferably ferritic stainless steel.

For example, the steel comprises between 60 wt.% and 80 wt.% of iron based on the total weight of the steel, preferably between 63 wt.% and 75 wt.% of iron.

- 5 For example, the steel comprises between 11 wt.% and 18 wt.% of chromium based on the total weight of the steel, preferably between 12 wt.% and 17 wt.%.

For example, the steel comprises between 10 wt.% and 14 wt.% of nickel based on the total weight of the steel, preferably between 11 wt.% and 13 wt.%.

10

For example, the steel comprises between 1 wt.% and 3 wt.% of molybdenum, such as 2 wt.% of molybdenum.

- 15 For example, the steel comprises less than 0.15 wt.% of carbon based on the total weight of the steel, preferably less than 0.12 wt.%.

For example, the steel comprises between 60 wt.% and 80 wt.% of iron, between 11 wt.% and 18 wt.% of chromium and less than 0.15 wt.% of carbon, based on the total weight of the steel.

20

For example, the steel comprises at least 60 wt.% of iron and between 11 wt.% and 18 wt.% of chromium based on the total weight of the steel. With preference, the steel also comprises less than 0.15 wt.% of carbon based on the total weight of steel; preferably less than 0.12 wt.%.

25

In particular, the steel comprises at least 60 wt.% of iron, between 11 wt.% and 18 wt.% of chromium, and less than 0.15 wt.% of carbon, based on the total weight of the steel. More particularly, the steel comprises at least 60 wt.% of iron, between 11 wt.% and 18 wt.% of chromium, less than 0.15 wt.% of carbon, between 10 wt.% and 14 wt.% of nickel and between
30 1 wt.% and 3 wt.% of molybdenum, based on the total weight of the steel

Advantageously, the anode has a thickness ranging between 3 mm and 6 mm as designed by SolidWorks software, preferably between 3.5 mm and 5.5 mm. A reactor housing, made for example in Inconel or steel, can encompass the anode, such as an anode made of copper.

35

When the anode is made of steel, there is no need of reactor housing. Therefore, the thickness of the whole reactor is ranging between 1 cm and 2 cm. As no reactor housing is required, the

reactor is lighter compared to a reactor with an anode in copper which required an Inconel or a steel housing.

For example, the anode is non-porous.

5 Advantageously, the one or more dehydrogenation catalysts comprise one or more metal-based catalysts, one or more metal oxide-based catalysts, one or more zeolites, one or more transition metal carbides, one or more transition metal nitrides, one or more carbon nanotubes, or any mixtures thereof. With preference, the one or more dehydrogenation catalysts comprise one or more metal-based catalysts, one or more metal oxide-based catalysts, one or more
10 zeolites, or any mixtures thereof. For example, the one or more zeolites are selected from the group of CHA, MFI families or any mixtures thereof. For example, the one or more zeolites are doped with one or metals selected from Mo, W, Fe, V, Cr or any mixtures thereof. For example, the one or more metal-based catalysts and/or the one or more metal oxide-based catalyst comprises one or more metals selected from Pd, Pt, Sn, Mo, W, Fe, V, Cr or any
15 mixtures thereof. The metal-based catalysts, such as the catalysts comprising one or more metals selected from Pd, Pt, Sn, Mo, W, Fe, V, Cr or any mixtures thereof, or preferably selected from Pd, Pt, Sn or any mixture thereof, are preferred as dehydrogenation catalysts. Such metal-based catalysts can be supported, for example onto Al₂O₃, SiO₂, TiO₂, CeO₂ or any mixture thereof, more preferably Al₂O₃ and/or SiO₂.

20

The fact that the anode comprises the one or more dehydrogenation catalysts allows for maximisation of the contact surface between the one or more dehydrogenation catalysts and the electrolyte, leading therefore to an improvement of the extraction capability of the membrane.

25

The electrolyte layer

The electrolyte layer acts as a proton transport layer. It is noted that since the electrolyte is a medium containing ion and that is electrically conducting upon the movement of those ions, the alkanes such as the propane, or the products of the dehydrogenation reaction, namely the
30 corresponding alkenes, such as the propene, cannot cross the electrolyte layer. Only the hydrogen under the form of proton (H⁺) will be able to cross the electrolyte layer and then extracted upon application of an electrical current.

For example, the electrolyte of the electrolyte layer comprises one or more perovskite
35 materials with an electrical conductivity ranging between 10⁻⁴ S/cm and 10⁻³ S/cm as determined by electrochemical impedance spectroscopy measurements performed at 600°C under an atmosphere comprising Ar and H₂ in a ratio 75/25.

For example, the electrolyte of the electrolyte layer comprises one or more perovskite materials having a general formula ABX_3 , wherein A and B are cations with different oxidation states and X is an anion. The A-cation occupies the center of the unit cell, while the B cation and the X anions (commonly oxygen) are arranged at the corners and the edges of the unit cell, respectively.

For example, the electrolyte of the electrolyte layer is or comprises one or more perovskite materials with one or more cations selected from Ba, Ce, Zr, Y, La, Sr, Mn, Fe, Eu, Tb, Ni, Yb, Pr, Sm, Zn, Gd, Er, Co, Nd, or any mixtures thereof. With preference, said one or more cations are selected from Ba, Ce, Zr, Y, Ni, or any mixtures thereof. More preferably, the one or more cations are selected from Ba, Ce, Zr, Y, or any mixtures thereof. For example, the electrolyte of the electrolyte layer is or comprises at least two perovskite materials, preferably in the form of a solid solution.

For example, the electrolyte of the electrolyte layer comprises one or more perovskite materials being $BaCeO_3$ and $BaZrO_3$ in the form of a solid solution. $BaCeO_3$ exhibits higher proton conductivity than $BaZrO_3$, but can suffer chemical instability. On the other hand, $BaZrO_3$ presents adequate stability under different conditions but presents a significant grain boundary resistance in addition to the high sintering temperature that causes Ba evaporation and the subsequent loss of transport properties. The solid solution of both $BaCeO_3$ and $BaZrO_3$, corresponding to the electrolyte $BaCe_{0.3}Zr_{0.5}Y_{0.2}O_3$, can overcome the disadvantages of both materials taken independently.

Advantageously, the electrolyte layer has a thickness ranging between 20 μm and 40 μm as determined by scanning electron microscopy, preferably between 25 μm and 35 μm .

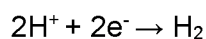
With preference, the anode, which is an anode, comprises one or more channels arranged in parallel to each other, each of said channels comprising the one or more dehydrogenation catalysts. For example, the anode can advantageously comprise two channels, preferably 4 channels, more preferably 8 channels, or 9 channels or 10 channels. A configuration in which an anode comprises 4 channels is schematized in figure 3. The fact that the one or more dehydrogenation catalysts are surrounded by the electrolyte further contributes to the extractive capabilities of the proton-conducting catalytic membrane of the present disclosure.

For example, each of said one or more channels has a cross-section amounting to at least 2 cm^2 , or to at least 2.5 cm^2 . For example, at least a part of said one or more channels are rectangular channels (see figure 4), flared depth channels (see figure 5), flared width

channels, bended channels, or corrugated channels; more preferably, all of said one or more channels are rectangular channels, flared depth channels, flared width channels, bended channels, or corrugated channels; even more preferably, all of said one or more channels are rectangular channels or flared depth channels, most preferably, all of said one or more channels are flared depth channels. In particular, flared depth channels are channels with a surface area of the outlet larger than the surface area of the inlet, the inlet and the outlet being defined according to the sense of the feed flow, for example the inlet is where the compound to be dehydrogenated (e.g., the propane) is introduced into the proton-conducting catalytic membrane and the outlet is where the one or more products of the dehydrogenation reaction (e.g., propylene, cracked products (such as ethane and/or methane), coke) are exiting the proton-conducting catalytic membrane.

The porous cathode

For example, the porous cathode comprises a mixture of an electrolyte and one or more second metals. This porous layer ensures the recombination of protons (H^+) into hydrogen (H_2), following the chemical equation (2):



With preference, the one or more second metals are selected from Ni, Fe, Co, Pd, Pt, or any mixtures thereof, more preferably Ni. For example, the amount of the one or more second metals is ranging between 50 wt.% and 70 wt.% of the total weight of said mixture, more preferably between 55 wt.% and 65 wt.%. Thus, in the case where nickel would be selected as the preferred cathodic metal, the amount of nickel in the mixture forming the porous cathode is ranging between 50 wt.% and 70 wt.% of the total weight of said mixture, more preferably between 55 wt.% and 65 wt.%.

Advantageously, the porous cathode is a porous layer with a thickness ranging between 30 μm and 50 μm as determined by scanning electron microscopy, preferably between 35 μm and 45 μm .

The proton-conducting catalytic membrane

The proton-conducting membrane conducts protons versus electrons.

Advantageously, the proton-conducting catalytic membrane of the present disclosure has a hydrogen extraction ratio ranging between 0.20 and 0.99, or between 0.25 and 0.90, at a temperature of at least 500°C and/or at a pressure of at most 0.1 MPa; the hydrogen extraction ratio being simulated by computational fluid dynamics (CFD) and/or quantified by gas chromatography (GC) during the reaction. With preference, the proton-conducting catalytic

membrane presents a hydrogen extraction ratio ranging between 0.20 and 0.99, or between 0.25 and 0.90, at a temperature of at least 550°C and/or at a pressure of at most 0.05 MPa.

For example, the hydrogen extraction ratio can be of at least 0.2 at least 550°C, the hydrogen extraction ratio being simulated by computational fluid dynamics (CFD), or the hydrogen extraction ratio can be of at least 0.5 at least 575°C.

Advantageously, the proton-conducting catalytic membrane can be a co-ionic catalytic membrane. Figure 6 displays a representation of the mechanism involving a co-ionic catalytic membrane. When a co-ionic membrane is used, water is co-fed with the feedstream (such as the feedstream of propane). The water is injected through the cathode side, namely the porous layer of catalytic membrane, so that the water is split into hydrogen and oxygen. Then the oxygen anions can cross the membrane, so as to react with part of the hydrogen that is formed at the anode side which is the electroconductive layer of the catalytic membrane. Such catalytic membrane conducts therefore protons versus electrons and oxygen anions and can therefore be referred to as a co-ionic catalytic membrane. Typical materials suitable for the co-ionic catalytic membranes are perovskites ABO_3 , such as oxides of Co, oxides of CoFe, oxides of Zr, oxides of BaZr, oxides of CaZr doped with one or more of Sr, Ba, Co, Cu, Fe, Cr, La, Ni, Ca.

With preference, the control of the quantity of coke that is formed can also occur when water is co-fed with the feedstream (such as the feedstream of propane), and without the co-ionic catalytic membrane, but only in presence of the proton-conducting catalytic membrane.

The dehydrogenation reactor

The present disclosure also relates to a dehydrogenation reactor comprising at least one proton-conducting catalytic membrane.

With preference, the dehydrogenation reactor has a planar geometry, reducing subsequently the gas polarization inside the reactor. It is therefore possible to further improve the extracting capability of the proton-conducting catalytic membrane of the present disclosure. Such dehydrogenation reactor further minimizes coking formation and therefore preserves the activity of the one or more dehydrogenation catalysts.

A method for preparing the dehydrogenation reactor is also described. Said method of preparation comprises the following steps:

- a) providing a reactor, preferably a reactor with a planar geometry;
- b) inserting the proton-conducting catalytic membrane as defined above within said reactor.

5 For example, when said dehydrogenation reactor comprises more than one proton-conducting catalytic membrane, said dehydrogenation reactor further comprises a spacer between each proton-conducting membrane. For example, the spacer is an electroconducting plate, preferably a steel plate, more preferably a stainless steel plate, even more preferably a ferritic stainless steel plate. For example, the steel plate is doped with one or more oxides (such as
10 oxides of La and/or Y), one or more metals, (such as metals selected from Au, Ni, Pt, Cu, Pd, Ti, W or a mixture thereof), one or more metallic alloys (such as one or more ferritic alloys and/or one or more chromite alloys) or a mixture thereof. The dehydrogenation reactor can thus be advantageously an arrangement of several proton-conducting catalytic membranes. For example, the arrangement of several proton-conducting catalytic membranes can
15 comprise two or more proton-conducting catalytic membranes, preferably between 4 and 20 proton-conducting catalytic membranes.

The several proton-conducting catalytic membranes can be arranged on top of each other, so as in figure 7 (namely a stacking of 4 membranes) or in figure 8 (namely a stacking of 20
20 membranes), or in an adjacent manner, wherein each proton-conducting catalytic membranes can be arranged next to each other on the same level. In another configuration, the several proton-conducting catalytic membranes can be arranged both on top of each other and in an adjacent manner.

25 Advantageously, said reactor has an inlet and an outlet, and said reactor is remarkable in that the inlet is in a first zone arranged so that a feed to said reactor via the inlet contacts the one or more dehydrogenation catalysts of the proton-conducting catalytic membrane before passing to the outlet, the outlet being for example in a second zone that is downstream of the proton-conducting catalytic membrane.

30

Advantageously, said reactor has an inlet and an outlet, and said reactor is remarkable in that the anode of the one or more proton-conducting catalytic membranes comprises one or more channels, each of said channels comprising the one or more dehydrogenation catalysts, and in that the inlet is in a first zone arranged so that a feed to said reactor via the inlet is conducted
35 through the one or more channels and contacts the one or more dehydrogenation catalysts before passing to the outlet being for example in a second zone that is downstream of the proton-conducting catalytic membrane.

With preference, the inlet has surface area identical to the surface area of the outlet or the inlet has a surface area smaller than the surface area of the outlet. More preferably, the inlet has a surface area smaller than the surface area of the outlet, which is the case when the channels within the anode are flared depth channels. For example, the surface area of the inlet can represent between 25% and 50% of the surface area of the outlet, preferably between 30% and 45%. In other words, the surface area of the outlet can be at least 2 times larger than the surface area of the inlet, more preferably at least 2.5 times, even more preferably at least 2.75 times, most preferably at least 3 times. This gradient in the geometry, wherein the lowest surface area is at the inlet side of the reactor and the bigger surface area is at the outlet side of the reactor, favours the extraction of hydrogen at the outlet side, in accordance with the circulation of the feed within the dehydrogenation reactor.

With preference, the inlet and outlet of the reactor are arranged on faces of the reactor that are opposed to each other. In other words, the inlet is in a first zone arranged so that a feed to said reactor via the inlet is conducted towards the proton-conducting catalytic membrane and the outlet is in a second zone that is downstream of the proton-conducting catalytic membrane. With preference, the first zone and the second zone each form one face of the reactor and are advantageously opposed to each other. Alternatively, the first zone and the second zone are arranged on a single face of the reactor, as shown by the stacking of figures 7 and 8.

With preference, said reactor has an additional inlet and an additional outlet arranged on faces opposed to each other. This additional inlet can be used for feeding a carrier gas, such as H₂, Ar, HarMix (*i.e.*, a mixture comprising H₂ and Ar with an amount of hydrogen comprised between 3 vol.% and 5 vol.% of the total volume of the mixture) or any mixtures thereof, to the dehydrogenation reactor.

Use of the proton-conducting catalytic membrane and/or of the dehydrogenation reactor

The disclosure further relates to the use of the proton-conducting catalytic membrane and/or of the dehydrogenation reactor in a dehydrogenation reaction, which can be a propane dehydrogenation reaction and/or an ethane dehydrogenation reaction, preferably a propane dehydrogenation reaction.

Test and determination methods

Scanning electron microscopy (SEM) analysis was carried out by using a field-emission scanning electron microscope using a Zeiss Ultra 55 fitted with a field emission gun using an accelerating voltage of 30.0 kV. All samples before the SEM characterization were covered with a conductive layer (Pt or Au).

- 5 Electrochemical Impedance Spectroscopy (EIS) measurements were performed to validate the transport properties of the developed membranes. EIS measurements were measured using a SolarTron instrument and by applying an electrical current through the membrane by means of two silver electrodes. EIS allows obtaining the resistance of the electrolyte, while equation (1) allows the determination of the electrical conductivity of the material.

$$10 \quad \sigma \left(\frac{S}{cm} \right) = \frac{1}{R (\Omega)} * \frac{t (cm)}{\phi (cm^2)} \quad (1)$$

wherein σ is the electrical conductivity, R is the electrical resistance and ϕ is the area of electrode and t is the thickness of the electrode.

- The hydrogen extraction ratio, which is the quantity of hydrogen extracted on the quantity of hydrogen formed, is obtained by simulations using computational fluid dynamics (CFD) technique and/or is determined by using gas chromatography (GC) technique. The hydrogen extraction ratio is calculated and/or determined on the basis of the reactant conversion, for example the propane conversion and in the case of GC, the quantity of hydrogen formed, or in the case of CFD, the theoretical quantity of hydrogen generated.

- With respect to the simulations made by CFD technique, they were performed with COMSOL Multiphysics 5.6 software on SYS-6018R-MTR Super server, with an Intel Xeon CPU E5-2640 v4 processor (clock speed 2.4 GHz, 40 CPUs) and 131 Gb RAM running Windows server edition 2016 (64-bit) as an operating system. For the gas flow, Navier-Stokes equations with the respective correction for the porous catalytic bed has been considered. Transport of species has been modelled using averaged-mixture model with propane, propylene and H₂ as species. The density of the gas mixture has been estimated considering a mixture of ideal gases, and the viscosity has been calculated using the Wilke model. The porosity and permeability are two key factors that govern the fluid flow in the porous region and the permeability for a packed bed with randomly distributed spherical particles was calculated using the Carman-Kozeny model. According to the publication of Tong Y. *et al* (*Int. J. of Hydrogen Energy*, **2022**, 47, 12067-12073), electrochemical hydrogen pumps are devices based upon proton-conducting electrolytes that offer 100% selectivity to hydrogen and allow for easy control of the hydrogen separation rate by simply adjusting the applied direct current. The tortuosity was estimated considering the inverse of the square root of the porosity. The binary gas diffusion coefficient has been calculated with an empirical equation based on the

Fuller kinetic gas theory, and it was corrected with the ratio of the porosity to tortuosity. The mesh performed was based on tetrahedral elements, where the element size was calibrated for fluid dynamics. The calculations were carried out using the Parallel Direct Solver (PARDISO) with parameter continuation to assure convergence. The relative tolerance of the method is 0.001. The selectivity in propylene ($C_3=$) is determined according to formula (2):

$$S_{propylene} = \frac{3 [C_3H_6]}{[CH_4] + 2[C_2H_4] + 2[C_2H_6] + 3[C_3H_6] + 3[C_3H_8]} \times 100 \quad (2)$$

wherein the numerator is the carbon adjusted molar amount of propylene and the denominator is the sum of all the carbons adjusted molar amount of all hydrocarbons in the effluent. Propylene yield was determined by multiplying the propane conversion with the propylene selectivity and divided by 100.

The thickness of the anode has been designed using SolidWorks software, which is a solid modelling computer-aided design (CAD) and computer-aided engineering (CAE) application published by Dassault Systems.

Examples

The embodiments of the present disclosure will be better understood by looking at the different examples below.

Preparation of the electrolyte $BaCe_{0.3}Zr_{0.5}Y_{0.2}O_3$ under a form of a solid solution of $BaCeO_3$ and $BaZrO_3$.

1) Grind the precursors separately for 60 hours. The employed precursors were: $BaCO_3$ (99.8% 1-micron powder. Alfa Aesar Ref: 14341, 1kg, CAS: 513-77-9), YSZ (ZrO_2/Y_2O_3) (8%), CeO_2 (REacton, 99.9% (REO), 5-micron powder. Alfa Aesar Ref: 11328, 1kg, CAS: 1306-38-3) and Y_2O_3 (99.9995%. ABCR Ref: AB102097, 100 g, CAS:1314-36-9).

2) Mix the different precursors in adequate proportions in acetone to fulfil the stoichiometry of the desired compound and grind for 24 hours. The following amount of precursors have been weighed:

$BaCO_3 \rightarrow 17.06$ g

YSZ $\rightarrow 6.14$ g

$CeO_2 \rightarrow 4.46$ g

$Y_2O_3 \rightarrow 1.09$ g

3) Dry by heating at 60 °C in a furnace.

4) Sieve the oxide mixture with a particle size of 200 μm .

5) The oxide mixture is uniaxially pressed at 40 kN in the shape of a disc (disc diameter: 30

mm).

6) Sinter discs at 1100°C for 10 hours.

7) Repeat steps 4-6 twice then, grind the mixture for 24 hours.

8) The calcined oxide mixture is pressed on 20 mm discs at 30kN.

5 9) Sinter the obtained discs at 1565°C for 12 hours.

Preparation of the cathode $\text{NiO-BaCe}_{0.3}\text{Zr}_{0.5}\text{Y}_{0.2}\text{O}_3$ under a form of a solid solution of BaCeO_3 and BaZrO_3

25 g of the solid solution of BaCeO_3 and BaZrO_3 is then mixed and ground for 15 hours in acetone together with 37.5 g of NiO (99% - metal basis; 325 mesh powder, Alfa Aesar Ref: 12359, 250 g, CAS 1313-99-1). After a step of drying by heating at 60°C in a furnace, the
10 mixed oxides are mixed with polyvinyl alcohol (PVA) to favour the pressing. The mixture has a ratio of mixed oxides/PVA 1/0.075. It is then ground with Agata's mortar before being pressed uniaxially at 40 kN in the shape of a disc (disc diameter: 20 mm). Optionally, the cathode is calcined at 700°C for 10 hours.

15 Then, the electrolytes are coated on the cathode by using screen-printing technique using a 21-mesh to obtain a porous cathode with an electrolyte layer. The support is a pressed powder transformed into a disk. In membranes, the screen-printing procedure consists of squeezing the slurry "ink" (electrolyte) to pass through a 21-mesh screen to print it on the cathode. After drying the layer (temperature of 80°C), it is possible to deposit extra layers. The typical
20 thickness of the obtained layer is around 30 μm . After that, the different layers and cathode are sintered at 1565 °C temperature to obtain an efficient attachment between the cathode and the electrolyte and to afford a sintered porous cathode with an electrolyte layer.

Prior to be used, the NiO species have been reduced under hydrogen to form Ni^+ . This activation step is carried out in a 25 vol.% H_2 atmosphere in argon at 700°C for 10 hours, optionally with a pre-calcination at 700°C under pure argon for 10 hours before the activation
25 step.

Preparation of the proton-conducting membrane

Then, an anodic layer is coated on the electrolyte layer of the sintered porous cathode.

30 The anodic layer is an anode comprising Ag. A silver conducting paint (DYNALOY® 342) was indeed obtained from Merck (CAS 7440-22-4) and painted by hand.

Figure 9 shows a representative example of the electrochemical impedance spectra used to calculate the electrical conductivity. Three batches proton-conducting membrane, namely of

electrochemical cells ($\text{BaCe}_{0.3}\text{Zr}_{0.5}\text{Y}_{0.2}\text{O}_3$ on uncalcined $\text{NiO-BaCe}_{0.3}\text{Zr}_{0.5}\text{Y}_{0.2}\text{O}_3$) layered with an Ag anode have been used. The curve “1” corresponds to wet conditions test (*i.e.*, 3 vol.% of water in the H_2/Ar feed) while the curves “2” and “3” are under the same dry conditions (*i.e.*, H_2/Ar feed without water) (reproducibility test). The tests have been made at 700°C . The intersect with the abscissa (that can be viewed on the zoom of figure 9 provided at figure 10) gives a value used for plotting figure 11.

Figure 11 shows the conductivity of three batches of proton-conducting membranes, namely of electrochemical cells (**1A**: $\text{BaCe}_{0.3}\text{Zr}_{0.5}\text{Y}_{0.2}\text{O}_3$ on uncalcined $\text{NiO-BaCe}_{0.3}\text{Zr}_{0.5}\text{Y}_{0.2}\text{O}_3$ with an activation preceded by a calcination; **1B**: $\text{BaCe}_{0.3}\text{Zr}_{0.5}\text{Y}_{0.2}\text{O}_3$ on uncalcined $\text{NiO-BaCe}_{0.3}\text{Zr}_{0.5}\text{Y}_{0.2}\text{O}_3$ with an activation without calcination; and **2A**: ($\text{BaCe}_{0.3}\text{Zr}_{0.5}\text{Y}_{0.2}\text{O}_3$ on calcined $\text{NiO-BaCe}_{0.3}\text{Zr}_{0.5}\text{Y}_{0.2}\text{O}_3$) layered with an Ag anode.

1A: $\text{NiO-BaCe}_{0.3}\text{Zr}_{0.5}\text{Y}_{0.2}\text{O}_3$ is pre-calcined at 700°C under pure argon for 10 hours before NiO being activated with a 25 vol.% H_2 atmosphere in argon at 700°C for 10 hours.

1B: NiO is activated with a 25 vol.% H_2 atmosphere in argon at 700°C for 10 hours, without a pre-calcination step.

2A: $\text{NiO-BaCe}_{0.3}\text{Zr}_{0.5}\text{Y}_{0.2}\text{O}_3$ is pre-calcined at 700°C under pure argon for 10 hours before addition of $\text{BaCe}_{0.3}\text{Zr}_{0.5}\text{Y}_{0.2}\text{O}_3$. Then the NiO is reduced under H_2 at 700°C for 10 hours.

Preparation of the proton-conducting catalytic membrane

The preparation of the reactor assembly is made as following:

25 g of the solid solution of BaCeO_3 and BaZrO_3 is then mixed and ground for 15 hours in acetone together with 37.5 g of NiO (99% - metal basis; 325 mesh powder, Alfa Aesar Ref: 12359, 250 g, CAS 1313-99-1). After a step of drying by heating at 60°C in a furnace, the mixed oxides are mixed with polyvinyl alcohol (PVA) to favour the pressing. The mixture has a ratio of mixed oxides/PVA 1/0.075. It is then ground with Agata's mortar before being pressed uniaxially at 40 kN in the shape of a disc (disc diameter: 20 mm). Optionally, the cathode is calcined at 700°C for 10 hours.

Then, the electrolytes are coated on the cathode by using screen-printing technique using a 21-mesh to obtain a porous cathode with an electrolyte layer. The support is a pressed powder transformed into a disk. In membranes, the screen-printing procedure consists of squeezing the slurry “ink” (electrolyte) to pass through a 21-mesh screen to print it on the cathode. After drying the layer (temperature of 80°C), it is possible to deposit extra layers. The typical thickness of the obtained layer is around 30 μm . After that, the different layers and cathode

are sintered at 1565 °C temperature to obtain an efficient attachment between the cathode and the electrolyte and to afford a sintered porous cathode with an electrolyte layer.

Prior to be used, the NiO species have been reduced under hydrogen to form Ni⁺. This activation step is carried out in a 25 vol.% H₂ atmosphere in argon at 700°C for 10 hours, optionally with a pre-calcination at 700°C under pure argon for 10 hours before the activation step.

Then, an anodic layer is coated on the electrolyte layer of the sintered porous cathode.

The anodic layer is an electroconductive layer comprising Cu, with channels and a dehydrogenation catalyst comprised within said channels.

10 The sintered porous cathode with an electrolyte layer is covered with copper, using ion-sputtering. The ion-sputtering conditions involve a Pfeiffer Classic 250 deposition system equipped with two RF (13.56 MHz) power sources, each capable of delivering up to 25 W of power. The system utilizes a Cu target for the deposition process and operates at room temperature. The deposition is carried out under a pure Ar atmosphere with a pressure range
15 of $2.6 \cdot 10^{-2}$ to $7.4 \cdot 10^{-2}$ mbar.

A channeled support in copper comprising a dehydrogenation catalyst is then prepared by 3D printing of the anode. The 3D printer is a Markforged MetalX printer using a Bound Powder Filament made of copper (90%) and a polymer (10%). The 3D printing allows to make linear channels. The obtained support is then calcined to remove the polymer at about 200°C and is
20 sintered under Ar at about 900°C for 72h. Then, the channels of the support are filled by hands with 1.25 g of catalyst powder, namely of PtSnEu support on Al₂O₃ (0.5 wt.% of Pt, 2 wt.% of Eu and 3 wt.% of Sn).

The sintered porous cathode with an electrolyte layer covered with copper is thus placed on top of the channeled anode comprising the dehydrogenation catalyst and sealed with either
25 GL1734 glass sealing paste (commercially available at Mo-Sci Corporation) or GM31107 glass sealant tape (commercially available at Schott AG) to obtain a proton-conducting catalytic membrane. The glass sealing paste is activated at 620°C for 4 hours, while the glass sealant tape is activated at 700°C for 2 hours.

The proton-conducting catalytic membrane is then placed into a reactor housing in Inconel
30 alloy (*i.e.*, a Ni/Cr alloy).

Hydrogen extraction with the proton-conducting catalytic membrane

The present disclosure introduces a reactor comprising an electrochemical cell based on protonic-conducting materials to extract the generated H₂ and shift the equilibrium to the propane dehydrogenation reaction.

The graph displayed in figure 12 shows the evolution of the electrical potential in function of the area specific resistance. The best operating cell potential is about 0.5 V and about 0.6 V, although it could be of 1.0 V or even more. However, the maximum value not to cross is 1.8 V, since above this limit, the proton-conducting catalytic membrane will be damaged.

The elemental model represented in figure 13 (in function of the temperature) and in figure 14 (in function of the pressure) shows that high current density, and therefore high H₂ extraction is required to achieve high propane conversions: at 550°C, the propane equilibrium conversion reaches around 30% for a conventional reactor where no extraction is occurring. The H₂ extraction led to clear conversion improvement, notably an extraction of 80 % of the H₂ generated is required to achieve conversions higher than 50%.

The H₂ extraction is modelled by considering the Faraday Law:

$$F_{H_2 \text{ extracted}} = \frac{i}{z \cdot F} \cdot M_{H_2} \quad (3)$$

wherein the $F_{H_2 \text{ extracted}}$ is the mass flux of the H₂ extracted for the H₂ extraction boundary, the i is the current density, the z is the exchanged electrons (two for the protonic exchange), F is the Faraday constant (96485 C/mol) and M_{H_2} is the H₂ molecular weight. Other lateral walls were assigned a no-slip boundary condition.

CFD simulations have been performed to study the different parameters affecting the PDH reaction and to optimize the reaction performance. To maximize the membrane surface area to catalyst volume ratio and improve the fluid dynamic regime, micro-channels have been placed in the reaction chamber, namely within the anode (of the proton-conducting catalytic membrane of the present disclosure. Those channels are either rectangular or flared depth.

One or more rectangular channels in the anode

The initial geometry considered in this study consists of a series of rectangular microchannels arranged in parallel, with a length of 50 mm and a surface area of the inlet being equal to the surface area of the outlet (e.g., 25 mm²), as shown by figure 4. These channels have been filled with 1.25 g of catalyst (i.e., PtSnEu supported on Al₂O₃) and equipped with a selective membrane to remove H₂ on the top surface.

Table 1 shows that the H₂ is evacuated from the membrane, subsequently leading to an increase of propane conversion by comparison with a dehydrogenation reactor devoid of the

proton-conducting catalytic membrane of the disclosure. The results of table 1 have been simulated by CFD at 550°C and at 0.1 MPa.

Table 1: Simulation by CFD of the propane conversion, using a proton-conducting catalytic membrane with one rectangular channel within the anode, as shown on figure 4.

	Feed flow F (Nml/min)	Space Velocity SV (Nml/h/g)	Maximum current density j (A/cm ²)	Propane conversion (%)
#1	17.4	750	0.45	52
#2	17.4	300	0.54	60
#3	8.7	750	0.25	55
#4	8.7	150	0.33	72

5

The maximum current density can be seen as the maximum hydrogen formed. As less propane is sent to the catalyst in experiment #3 compared to experiment #1, less hydrogen is formed and then less current is needed to extract this hydrogen. However, at similar conditions (same feed flow and same space velocity, a lower current density (as in experiment #1 versus experiment #2, as in experiment #3 versus experiment #4) does not allow a maximum extraction, meaning that the conversion is decreasing.

10

A lower feed flow allows generally to increase the propane conversion, since the catalyst has time to adsorb and activate more propane.

One or more flared depth channels in the anode

15 However, an optimized geometry study showed that the optimal extraction is performed having a flared depth channel as shown in figure 5, namely with a surface area of the outlet (e.g., 25 mm²) being larger than the surface area of the inlet (e.g., 10 mm²). In this experiment, the length of the channel has been fixed to 50 mm. These channels have been filled with 1.25 g of catalyst (i.e., PtSnEu supported on Al₂O₃).

20 Table 2 summarizes the results using a dehydrogenation reactor having an outlet with a surface area of 25 mm² and an inlet with a surface area of 10 mm². These results have been simulated at a pressure of 0.1 MPa and with a feed flow F of 8.7 Nml/min.

Table 2: Simulation by CFD of the propane conversion using a proton-conducting catalytic membrane with one flared depth channel within the anode, as shown on figure 5.

	Space Velocity SV (Nml/h/g)	Temperature (°C)	Maximum current density j (A/cm ²)	Propane conversion (%)	Propylene selectivity (%)
#5	750	450	0.13	29	99
#6	750	500	0.19	44	98
#7	750	550	0.25	57	96
#8	750	600	0.28	57	91
#9	750	650	0.28	73	80
#10	150	450	0.17	40	98
#11	150	500	0.24	58	96
#12	150	550	0.30	76	91
#13	150	600	0.33	87	84
#14	150	650	0.32	94	73

It has thus been demonstrated that lower temperatures lead to lower propane conversion and higher propylene selectivity.

It has also been demonstrated that lower space velocity leads to higher propane conversion but lower propylene selectivity and thus more cracking into ethane and methane.

Improvement over configuration devoid of H₂ extraction

Table 3 indicates the improvement of using a flared depth configuration, in comparison of a proton-conducting catalytic membrane using a rectangular channel configuration or without any proton-conducting catalytic membrane. The simulation has been made at a space velocity SV of 750 Nml/h/g.

Table 3: Simulation by CFD of the propane conversion and the hydrogen mole fraction at the outlet of the proton-conducting catalytic membrane.

		Feed flow F (Nml/min)	current density (A/cm ²)	Propane conversion (%)	Average H ₂ mole fraction at the outlet
#15	no extraction	8.7	0	28.45	0.176
		17.4	0	28.70	0.180
#16	H ₂ extraction using rectangular channels	8.7	0.25	48.80	0.052
		17.4	0.25	47.18	0.066
#17		8.7	0.25	54.57	0.094

	H ₂ extraction using flared depth channels	17.4	0.25	51.51	0.051
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It can be highlighted here that on the outlet side of the dehydrogenation reactor, the conversion of propane is reaching at least 50% when flared depth channels are present within the anode, while for a similar reactor devoid of the proton-conducting catalytic membrane of the disclosure, the conversion of propane is inferior to 30%.

Dehydrogenation conditions

Different dehydrogenating conditions including current intensities, feed flows and/or space velocities have been simulated as indicated in table 4 (at constant temperature) and in table 5 (at constant feed flow).

It is noted that when the dehydrogenating step is carried out at 550°C, acceptable side reactions occurred (> 95% selectivity).

Table 4: Dehydrogenating step carried out at 550°C.

	Optimum current intensities	Feed flows	Space velocities	Propane conversion
#18	0.25 A/cm ²	8.7 NmL/min	750 NmL/h/g	55%
#19	0.33 A/cm ²	8.7 NmL/min	150 NmL/h/g	72%
#20	0.45 A/cm ²	17.4 NmL/min	750 NmL/h/g	52%
#21	0.54 A/cm ²	17.4 NmL/min	300 NmL/h/g	60%

The highest quantity of formed H₂ anticipated by CFD simulations has been obtained without side reactions, at a feed flow of 17.4 NmL/min; space velocity of 300 NmL/H/g and current intensity of 0.54 A/cm² (see experiment 21). In such conditions, 10.44 NmL of H₂ formed which is below the extraction potential of the membrane for a single channel of 2.5 cm² prepared as an example: H₂ extraction of 5 NmL·min⁻¹·cm⁻² meaning 12.5 NmL/min. It showed that the extraction level reached by the disclosure is satisfying. Indeed, through perfect gas law, as it is normal flow rate then the normal volume is as follows 1 mmol = 22.4 ml. Given that the feed flow is 17.4 NmL/min, the number of moles is amounting to 0.78 mmol. As the conversion is 60% (see experiment 21), the volume of H₂ formed is 10.44 NmL.

Under the propane dehydrogenation conditions, the propane can be oxidized into propylene but also other compounds are formed, such as ethylene, ethane and methane. The selectivities were assessed in accordance with the conditions given in table 5.

Table 5: Dehydrogenating step carried out at a feed flow of 8.7 Nml/min

	Temperature	Optimum current intensities	Space velocities	Propane conversion	Propylene selectivity	Propylene yield
#22	450°C	0.13 A/cm ²	750 Nml/h/g	29%	99%	28.7%
#23	450°C	0.17 A/cm ²	150 Nml/h/g	40%	98%	39.2%
#24	500°C	0.19 A/cm ²	750 Nml/h/g	44%	98%	43.1%
#25	550°C	0.24 A/cm ²	150 Nml/h/g	58%	96%	55.7%
#26	550°C	0.25 A/cm ²	750 Nml/h/g	57%	96%	54.7%
#27	550°C	0.30 A/cm ²	150 Nml/h/g	76%	91%	69.2%
#28	600°C	0.28 A/cm ²	750 Nml/h/g	57%	91%	51.9%
#29	600°C	0.33 A/cm²	150 Nml/h/g	87%	84%	73.1%
#30	650°C	0.28 A/cm ²	750 Nml/h/g	73%	80%	58.4%
#31	650°C	0.32 A/cm ²	150 Nml/h/g	94%	73%	68.6%

Experiment #29 provides a yield in propylene of 73.1%.

Furthermore, the CFD simulation results have been plotted as propane conversion and propylene selectivity against the H₂ extraction ratio, for different temperatures and space velocities (SV). The flowrate has been set to 8.7 Nml/min, while the current density varied from 0 (no H₂ extraction) to a maximum value, which is indicated in table 5. This maximum value corresponds to the point where the H₂ molar fraction near the outlet becomes “negative”. Figure 15 shows the results for a space velocity of 150 Nml/h/g and figure 16 shows the results for a space velocity of 750 Nml/h/g.

As expected, H₂ extraction has a clear impact on conversion at relatively low temperatures. Indeed, below 600 °C the propane conversion could increase by 20-40 % depending on the

conditions. On the contrary, at higher temperatures (650 °C), the H₂ extraction has little impact on the conversion since the system becomes kinetically limited. However, a higher temperature leads to larger conversion values, but selectivity to propylene decreases.

Comparing the space velocities, for SV=150 (*i.e.*, higher catalyst loading), higher conversion values are obtained and H₂ extraction affects the conversion a little bit more since kinetic limitations are overcome. But increasing the catalyst loading has an important disadvantage: the activation of the side reactions leads to a lower propylene selectivity.

At SV of 150, an optimum was found between propylene selectivity and propane conversion at 550 °C, propylene selectivity could be over 90 % and propane conversion over 50 % if over 90 % of the H₂ produced is extracted (see #32 in table 6).

Table 6: Dehydrogenating step carried out in the best conditions

	Temperature	Current intensities	Feed flow	Space velocities	Propane conversion	Propylene selectivity
#32	550°C	0.30 A/cm ²	8.7 Nml/min	150 Nml/h/g	76%	91%

Experiment #32 provides a yield in propylene of 69.2%.

Preventing coke formation at temperature superior to 550°C

Figure 17 shows that the formation of coke from propylene is occurring at temperature above 550°C, reducing thus the selectivity into propylene. The formation of coke tends to increase at higher temperature, for example up to 7% of coke at a temperature of 650°C and at an H₂ extraction of 96%. The coking generates a loss of selectivity.

The coke deposition and further suppression were modeled by CFD simulations. The two solutions envisioned were water co-feeding and/or water co-feeding with use of a co-ionic membrane, as shown in table 7.

Table 7: Suppression of coke deposition by water co-feeding or water co-feeding along with use of a co-ionic membrane. Experiments were carried out at 575°C, with a current intensity of 0.1 A/cm² and a time on stream (TOS) of 100 h.

		No steam	Water-co-feeding		Addition of co-ionic membrane	
	Cross-section (cm)	Coke deposition (mg _{Coke} /g _{cat})	H ₂ O molar fraction (%)	Coke suppression (%)	H ₂ O molar fraction (%)	Coke suppression (%)
#33	0.10	0.37	2.76	100	0.1	20.5

#34	1.25	1.14	2.28	98.3	0.6	75.9
#35	2.50	1.27	2.07	98.1	1.2	92.8
#36	3.75	1.32	1.95	98.5	1.7	97.3
#37	4.90	1.35	1.86	98.8	2.1	98.7

Figure 18 shows a flared depth channels in which the line A was modelled into graphs showing the evolution of the amount of coke within the channels. Thus, figure 19 shows the evolution of the coke deposition in function of the reactor length in the absence of steam, while figure 20 shows the evolution of the coke suppression in function of the reactor length when water is co-fed with the propane and when the reactor employs a proton-conducting catalytic membrane in accordance with the disclosure and figure 21 shows the evolution of the coke suppression in function of the reactor length when water is co-fed with the propane and when the proton-conducting catalytic membrane of the reactor is a co-ionic membrane.

- Both solutions showed coke efficient suppression leading to very stable propylene yield for 100 hours on stream. In contrast, the absence of steam affords a significant drop in yield after 25 hours on stream.

Figures 22 to 24 show the evolution of the propylene yield in function of the time on stream (TOS).

- Figure 22 shows that the co-feeding of water into the stream comprising propane at a molar fraction of 2.7% allows to maintain the yield into propylene as about 40% at a current density of 0.1 A/cm².

- Figure 23 shows that the co-feeding of water into the stream comprising propane at a molar fraction of 5.4% allows to maintain the yield into propylene as about 50% at a current density of 0.2 A/cm².

Figure 24 shows that the co-feeding of water into the stream comprising propane at a molar fraction of 7.9% allows to maintain the yield into propylene as about 55% at a current density of 0.3 A/cm².

- Figure 25 is a view of the reactor assembly in which the anode is made of copper. An external steel housing is shown. The copper anode is for example incorporated within the external steel housing. The scheme shows the channels into the copper anode, that have been made using 3D printing. For example, the reactor assembly has a diameter of 17 cm and a height of 10 cm. The electrical connection to the copper anode must be made through the external steel housing.

Proton-conducting catalytic membrane with an anode in steel

The preparation of the reactor assembly (see figure 26) is made as following:

- 5 25 g of the solid solution of BaCeO₃ and BaZrO₃ is mixed and ground for 15 hours in acetone together with 37.5 g of NiO (99% - metal basis; 325 mesh powder, Alfa Aesar Ref: 12359, 250 g, CAS 1313-99-1). After a step of drying by heating at 60°C in a furnace, the mixed oxides are mixed with polyvinyl alcohol (PVA) to favour the pressing. The mixture has a ratio of mixed oxides/PVA 1/0.075. It is then ground with Agata's mortar before being pressed uniaxially at
10 40 kN in the shape of a disc (disc diameter: 20 mm). Optionally, the cathode is calcined at 700°C for 10 hours.

Then, the electrolytes are coated on the cathode by using screen-printing technique using a 21-mesh to obtain a porous cathode with an electrolyte layer. The support is a pressed powder transformed into a disk. In membranes, the screen-printing procedure consists of squeezing
15 the slurry "ink" (electrolyte) to pass through a 21-mesh screen to print it on the cathode. After drying the layer (temperature of 80°C), it is possible to deposit extra layers. The typical thickness of the obtained layer is around 30 µm. After that, the different layers and cathode are sintered at 1565 °C temperature to obtain an efficient attachment between the cathode and the electrolyte and to afford a sintered porous cathode with an electrolyte layer.

- 20 Prior to be used, the NiO species have been reduced under hydrogen to form Ni⁺. This activation step is carried out in a 25 vol.% H₂ atmosphere in argon at 700°C for 10 hours, optionally with a pre-calcination at 700°C under pure argon for 10 hours before the activation step.

Then, an anodic layer is coated on the electrolyte layer of the sintered porous cathode.

- 25 The anodic layer is an electroconductive layer of stainless steel, with channels and a dehydrogenation catalyst comprised within said channels.

The sintered porous cathode with an electrolyte layer is covered with copper, using ion-sputtering. The ion-sputtering conditions involve a Pfeiffer Classic 250 deposition system equipped with two RF (13.56 MHz) power sources, each capable of delivering up to 25 W of
30 power. The system utilizes a Cu target for the deposition process and operates at room temperature. The deposition is carried out under a pure Ar atmosphere with a pressure range of 2.6.10⁻² to 7.4.10⁻² mbar.

A channeled support in steel comprising a dehydrogenation catalyst is then prepared by deep drawing or machining. The fact that deep drawing or machining can be used to prepared the channeled support is advantageous in the sense that it avoids the use of the 3D printing technique. A steel plate and quartz wool are used around the catalyst channels to avoid the catalyst to move. GM31107 glass sealant tape (commercially available at Schott AG) is used to sealed the steel plate to the steel support. The glass sealing tape is activated at 700°C for 2 hours.

Then, the channels of the support are filled by hands with 1.25 g of catalyst powder, namely of PtSnEu support on Al₂O₃ (0.5 wt.% of Pt, 2 wt.% of Eu and 3 wt.% of Sn).

The sintered porous cathode with an electrolyte layer covered with copper is thus placed on top of the channeled support comprising the dehydrogenation catalyst and sealed with either GL1734 glass sealing paste (commercially available at Mo-Sci Corporation) or Cotronics Resbond® 908 paste (*i.e.*, an alumina-based bonding ceramic cement) to obtain a proton-conducting catalytic membrane. The glass sealing paste is activated at 620°C for 4 hours, while the Cotronics tape is cured 24 h at room temperature with applied weight.

Finally, an upper steel piece with channels is added to the channeled support and proton-conducting catalytic membrane. Then both steel pieces are sealed together using either GL1734 glass sealing paste (commercially available at Mo-Sci Corporation) or Cotronics Resbond® 908 paste (*i.e.*, an alumina-based bonding ceramic cement) to obtain a proton-conducting catalytic membrane. The glass sealing paste is activated at 620°C for 4 hours, while the Cotronics tape is cured 24 h at room temperature with applied weight.

A closed membrane reactor is thus obtained (see figures 26 and 27). As the steel anode comprises the channels, the risks of leaks are decreased once the reactor has been completed. The shape of the steel anode allows for having electrical connections on the side of the membrane, which facilitates their access. This is advantageous in comparison with a reactor assembly with a reactor housing made of Inconel, since in this case, the electrical connections cannot be in contact with the Inconel to ensure an adequate connection.

CLAIMS

1. A proton-conducting catalytic membrane is **characterized in that** it comprises an anode, an electrolyte layer disposed on top of the anode and a porous cathode disposed on top of the electrolyte layer, wherein the anode comprises at least one dehydrogenation catalyst and is devoid of pores, and wherein the electrolyte layer comprises one or more perovskite materials with one or more cations selected from Ba, Ce, Zr, Y, La, Sr, Mn, Fe, Eu, Tb, Ni, Yb, Pr, Sm, Zn, Gd, Er, Co, Nd, or any mixtures thereof.
2. The proton-conducting catalytic membrane according to claim 1 is characterized in that the anode is made of one or more first metals and/or of one or more spinels.
3. The proton-conducting catalytic membrane according to claim 2 is characterized in that the one or more first metals are selected from Cu, Fe, Cr, Ag, Ni, Mo, Pt, Pd, Au, Mn or any mixtures thereof.
4. The proton-conducting catalytic membrane according to any one of claims 1 to 3 is characterized in that the anode is made of or comprises steel.
5. The proton-conducting catalytic membrane according to claim 4 is characterized in that the anode is made of or comprises stainless steel.
6. The proton-conducting catalytic membrane according to claim 3 or 5 is characterized in that the steel comprises at least 60 wt.% of iron and between 11 wt.% and 18 wt.% of chromium based on the total weight of the steel.
7. The proton-conducting catalytic membrane according to claim 6 is characterized in that the steel also comprises less than 0.15 wt.% of carbon based on the total weight of steel.
8. The proton-conducting catalytic membrane according to any one of claims 1 to 7 is characterized in that the one or more dehydrogenation catalysts comprise one or more metal-based catalysts, one or more metal oxide-based catalysts, one or more zeolites, one or more transition metal carbides, one or more transition metal nitrides, one or more carbon nanotubes, or any mixtures thereof.

9. The proton-conducting catalytic membrane according to any one of claims 1 to 8 is characterized in that the electrolyte layer comprises one or more perovskite materials with an electrical conductivity ranging between 10^{-4} S/cm and 10^{-3} S/cm as determined by electrochemical impedance spectroscopy measurements performed at 600°C under an atmosphere comprising Ar and H₂ in a ratio 75/25.
10. The proton-conducting catalytic membrane according to any one of claims 1 to 9 is characterized in that the proton-conducting catalytic membrane is a co-ionic catalytic membrane.
11. The proton-conducting catalytic membrane according to any one of claims 1 to 10 is characterized in that the porous cathode comprises a mixture of one or more electrolytes and one or more **second metals**.
12. The proton-conducting catalytic membrane according to claim 11 is characterized in that the one or more second metals are selected from Ni, Fe, Co, Pd, Pt, or any mixtures thereof and/or the amount of said one or more second metals is ranging between 50 wt.% and 70 wt.% of the total weight of said mixture.
13. A dehydrogenation reactor is characterized in that it comprises at least one proton-conducting catalytic membrane as defined in accordance with any one of claims 1 to 12.
14. The dehydrogenation reactor according to claim 13 is characterized in that the dehydrogenation reactor has a planar geometry.
15. The dehydrogenation reactor according to claim 13 or 14 is characterized in that it comprises an arrangement of at least two proton-conducting catalytic membranes arranged on top of each other and/or it comprises an arrangement of at least two proton-conducting catalytic membranes which are coplanar with each other.
16. The dehydrogenation reactor according to claim 15 is characterized in that said dehydrogenation reactor further comprises a spacer between each proton-conducting catalytic membrane.
17. The dehydrogenation reactor according to any one of claims 13 to 16, wherein said reactor has an inlet and an outlet, said reactor being characterized in that the inlet is in a first zone arranged so that a feed to said reactor via the inlet contacts the one or

more dehydrogenation catalysts of the one or more proton-conducting catalytic membranes before passing to the outlet being in a second zone that is downstream of the one or more proton-conducting catalytic membranes.

5 18. The dehydrogenation reactor according to any one of claims 13 to 17, wherein said reactor has an inlet and an outlet, said reactor being characterized in that the anode of the one or more proton-conducting catalytic membranes comprises one or more channels, each of said channels comprising the one or more dehydrogenation catalysts, and in that the inlet is in a first zone arranged so that a feed to said reactor
10 via the inlet is conducted through the one or more channels and contacts the one or more dehydrogenation catalysts before passing to the outlet being in a second zone that is downstream of the one or more proton-conducting catalytic membranes.

15 19. The dehydrogenation reactor according to claim 17 or 18, characterized in that the inlet has a surface area identical to the surface area of the outlet.

20 20. The dehydrogenation reactor according to claim 17 or 18, characterized in that the inlet has a surface area smaller than the surface area of the outlet.

21. A method for making a proton-conducting catalytic membrane as defined according to any one of claims 1 to 12 is characterized in that said method comprises the following steps:

- 25 a) providing a mixture of one or more electrolytes and one or more second metals to form a solution of mixed oxides;
b) pressing uniaxially the mixture provided at step (a) to form a porous cathode;
c) optionally, calcining said porous cathode
d) providing one or more electrolytes;
30 e) screen-printing said one or more electrolytes on the porous cathode or on the calcined porous cathode if step (c) is carried out, to obtain an electrochemical cell with an electrolyte layer;
f) sintering said electrochemical cell;
g) providing an anode made of one or more first metals and/or of one or more spinels;
35 h) depositing at least one dehydrogenation catalyst on said anode provided at step (g), so as to form a catalytic anode;

- i) assembling together the electrochemical cell of step (f) with the catalytic anode formed at step (h), so as to obtain a proton-conducting catalytic membrane as defined according to any one of claims 1 to 12.

- 5 22. The method according to claim 21 characterized in that before step (a), an activation step is carried out under activation conditions on the oxidized form of the one or more second metals.
- 10 23. The method according to claim 22, characterized in that a calcination step is carried out before said activation step.
- 15 24. The method according to any one of claims 21 to 23 is characterized in that before step (h) a step of forming one or more channels within the anode provided at step (g) is carried out.
- 20 25. The method according to claim 24, characterized in that said step of forming one or more channels is performed by electroforming or electroplating the anode provided at step (g).
- 25 26. The method according to any one of claims 21 to 25 is characterized in that before step (i), a step of covering the electrochemical cell of step (f) with a layer of the same one or more first metals as those making the anode provided at step (g) is carried out.
- 30 27. The method according to any one of claims 21 to 26 is characterized in that the step (i) is performed by sealing together the electrochemical cell of step (f) with the catalytic anode formed at step (h) with one or more sealants.
- 35 28. The use of a proton-conducting catalytic membrane as defined in any one of claims 1 to 12 and/or of a dehydrogenation reactor as defined in any one of claims 13 to 20 in a dehydrogenation reaction.
29. Use according to claim 28, carried out in a propane dehydrogenation reaction
30. Use according to claim 28 or 29, carried out in an ethane dehydrogenation reaction.

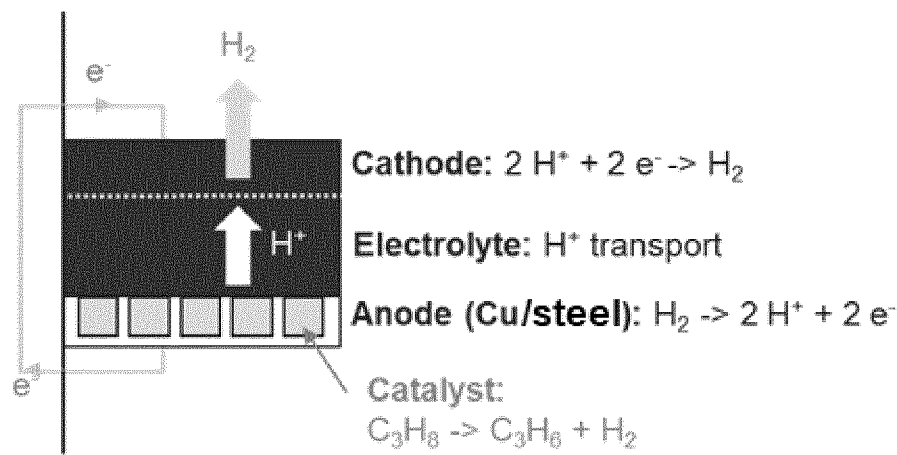


Fig. 1

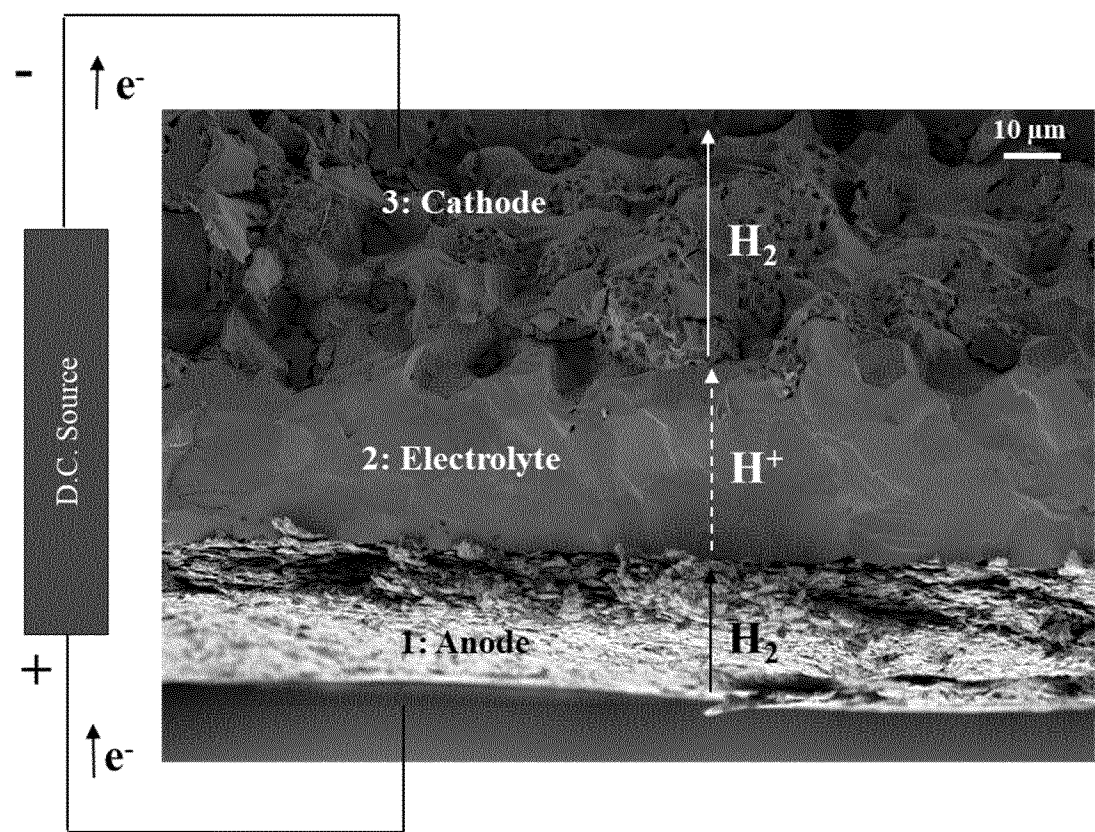


Fig. 2

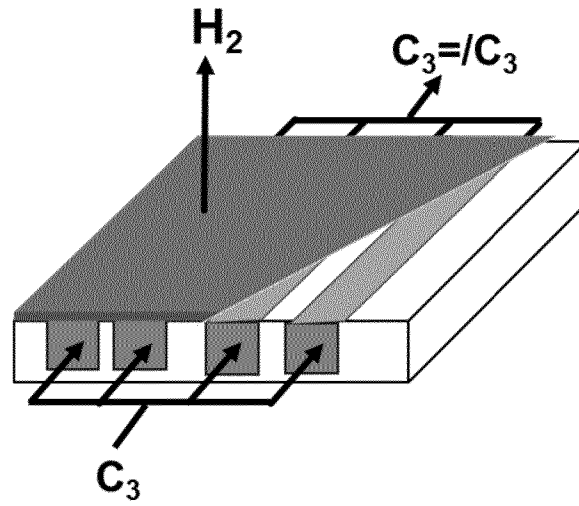


Fig. 3

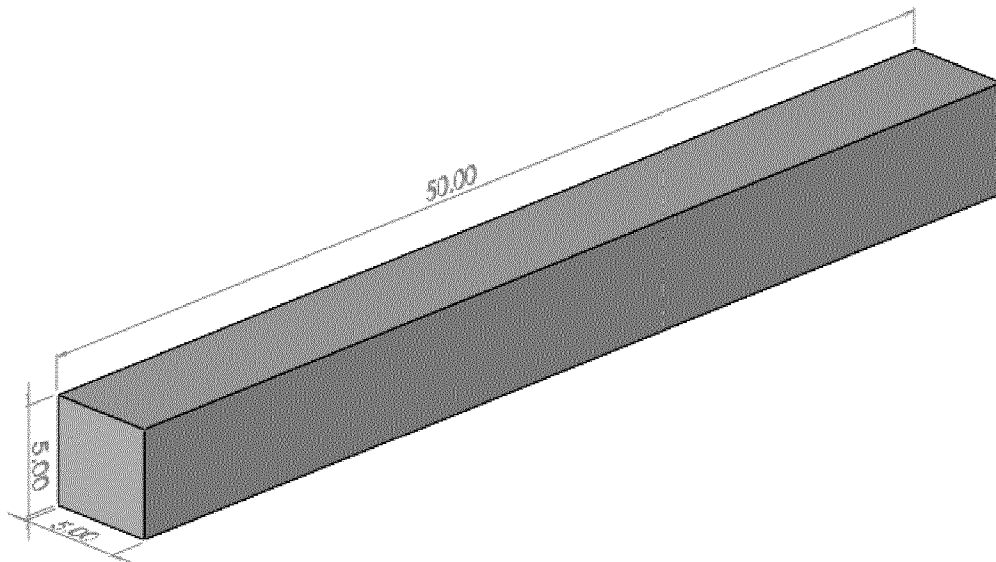


Fig. 4

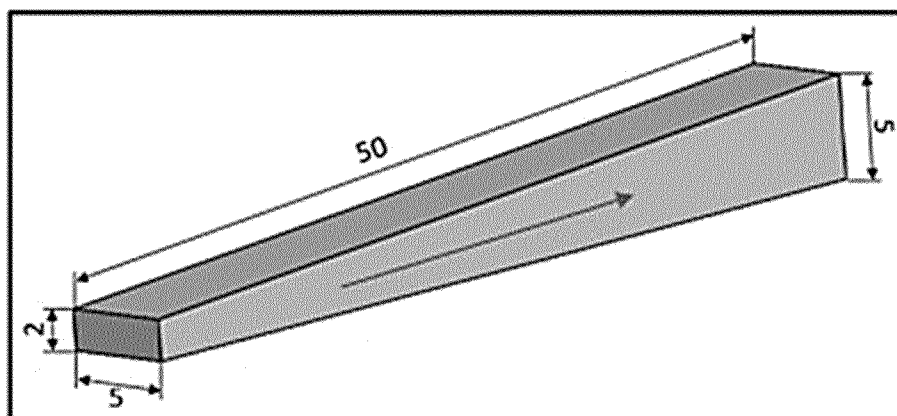


Fig. 5

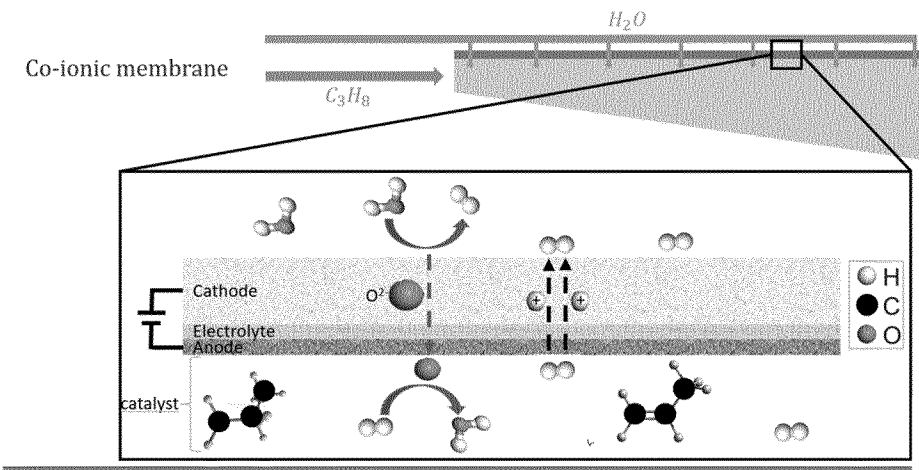


Fig. 6

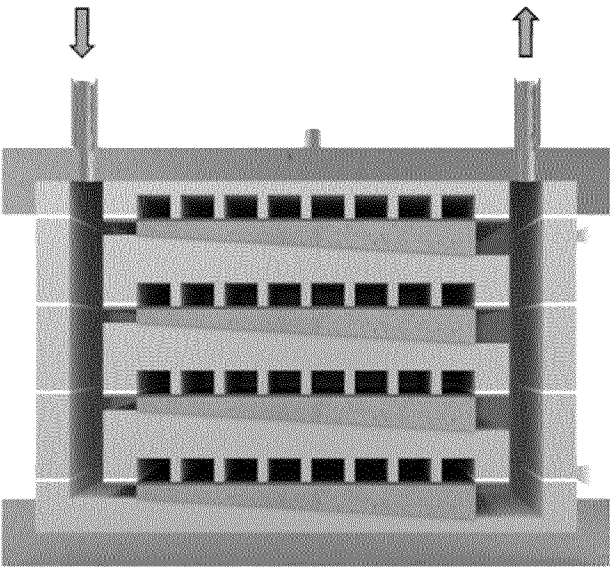


Fig. 7

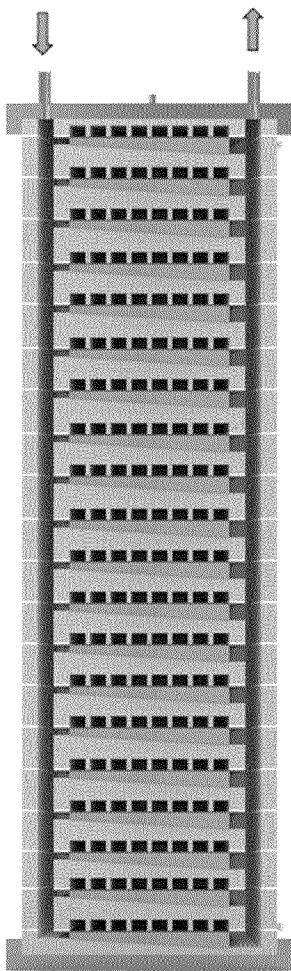


Fig. 8

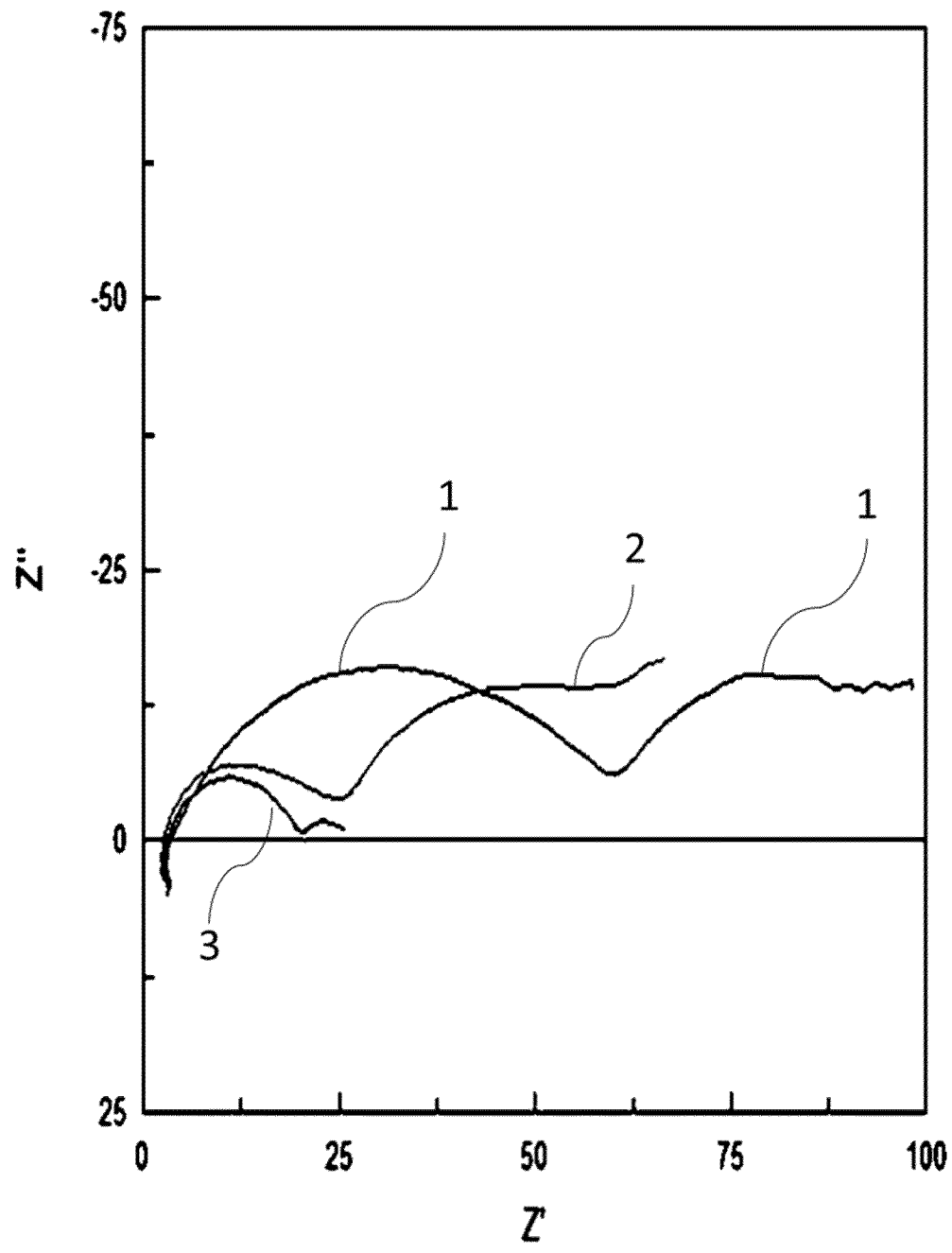


Fig. 9

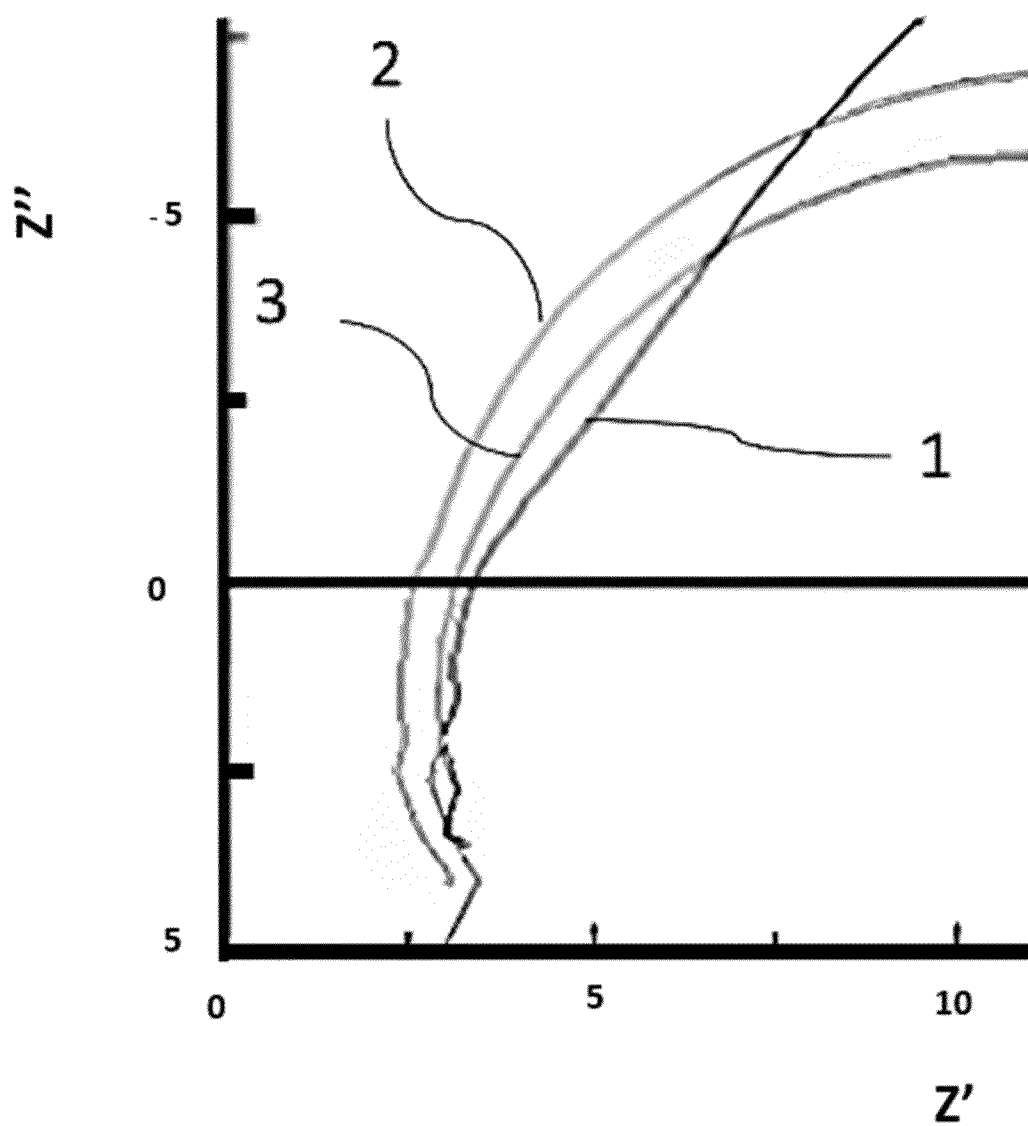


Fig. 10

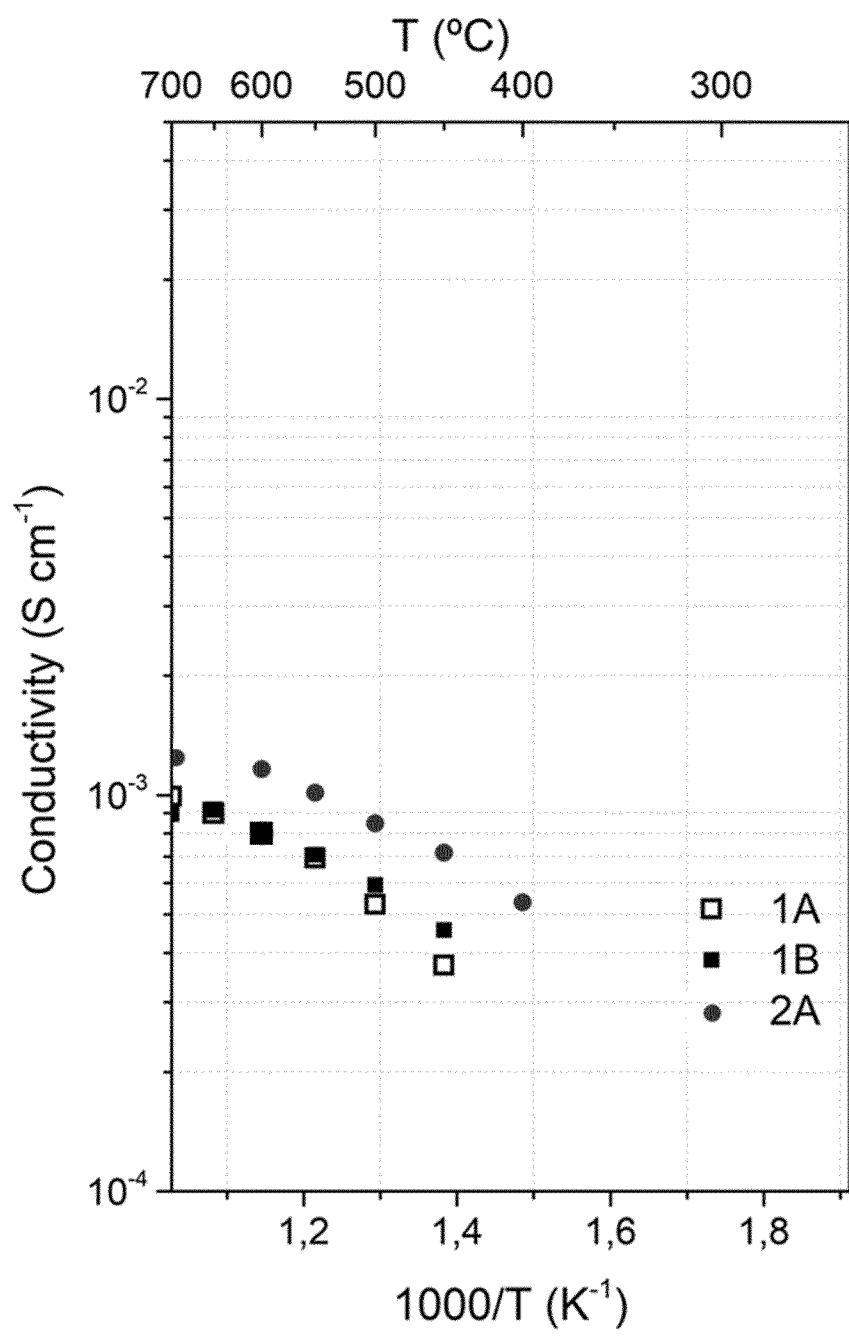


Fig. 11

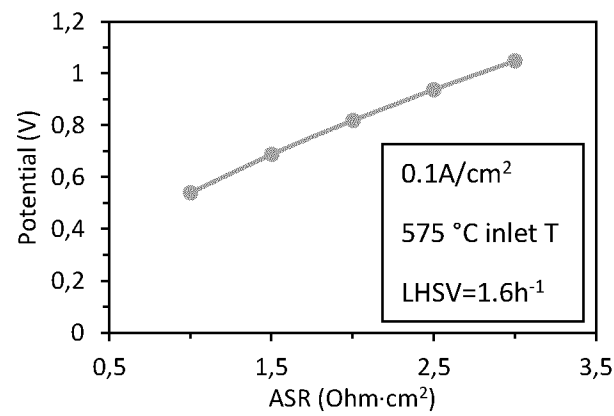


Fig. 12

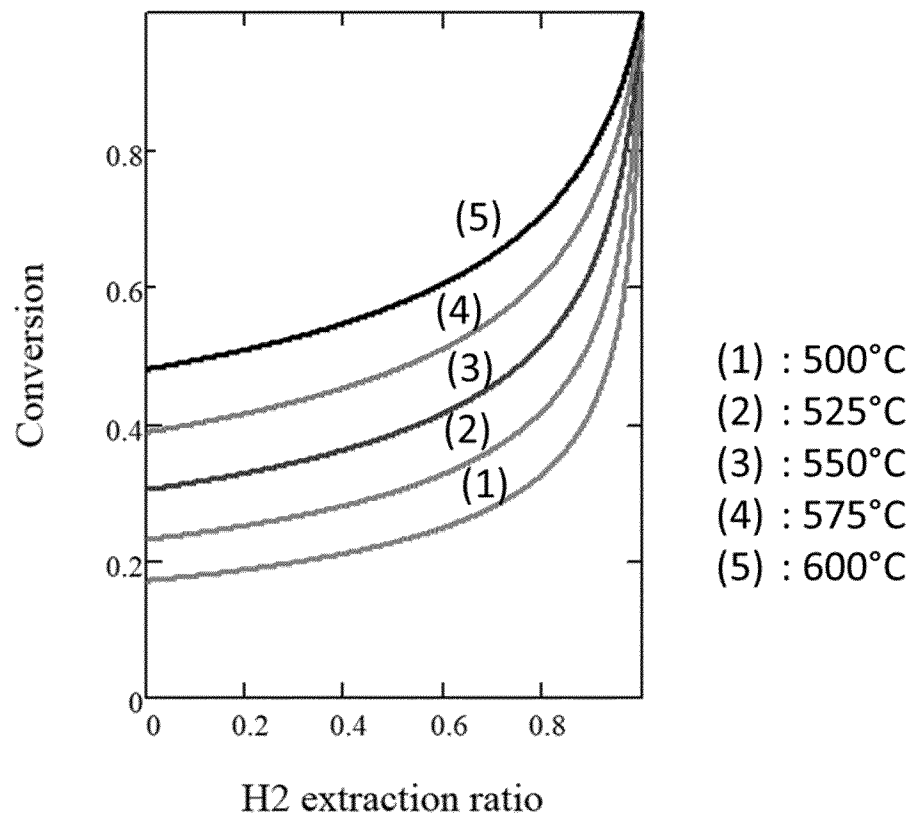


Fig. 13

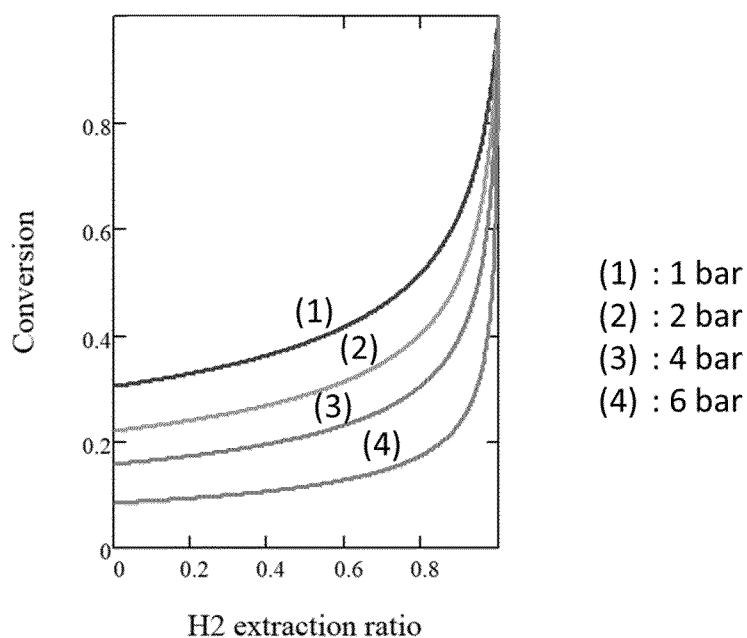


Fig. 14

SV = 150 Nml/h/g

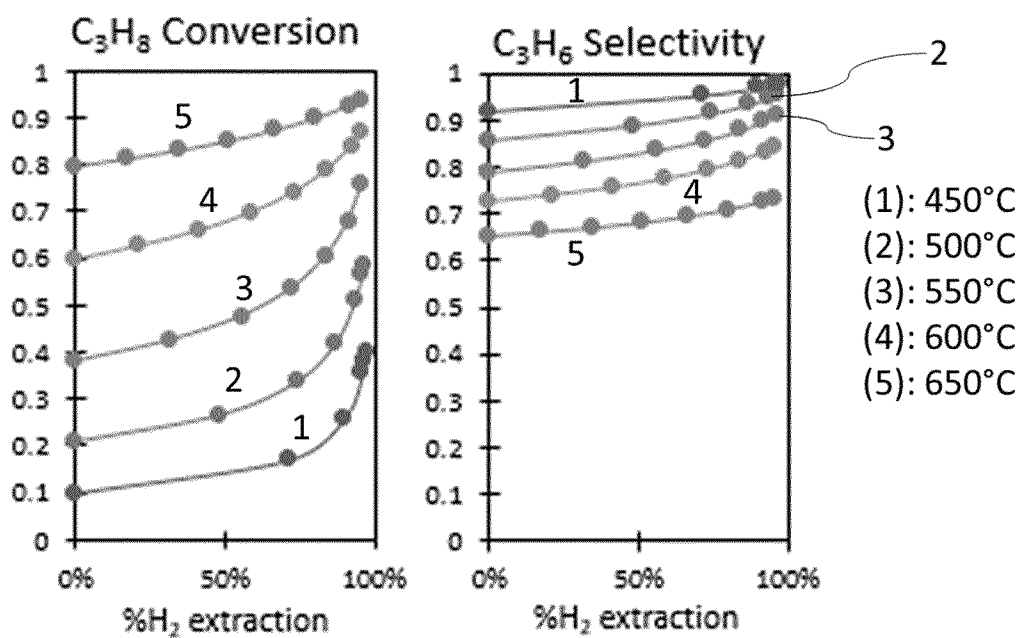


Fig. 15

SV = 750 Nml/h/g

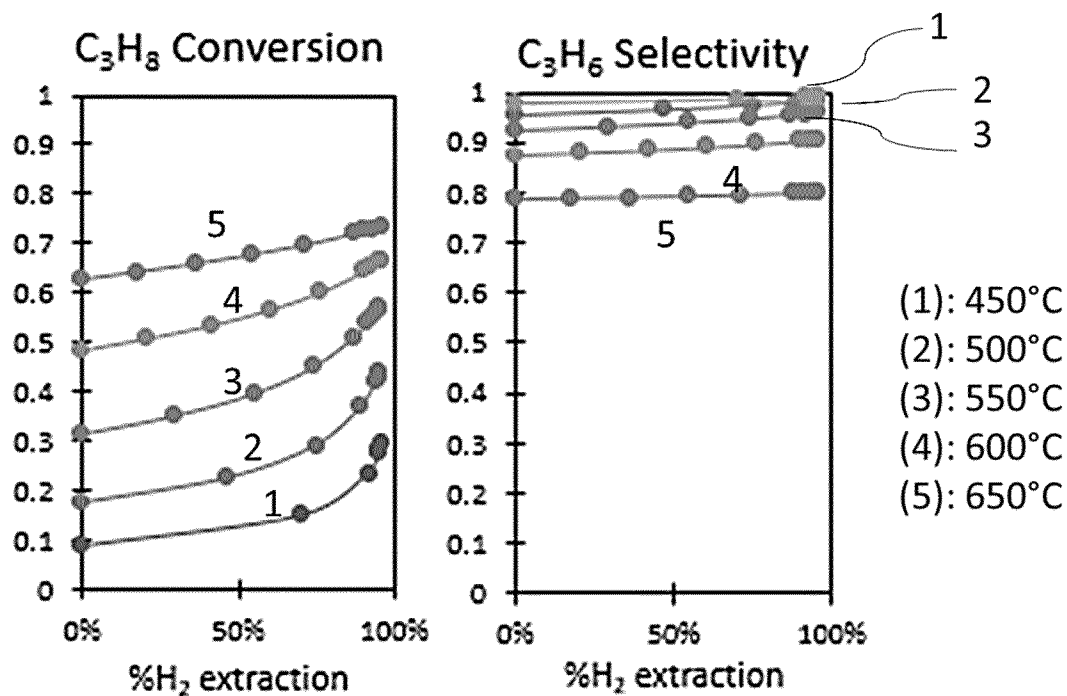
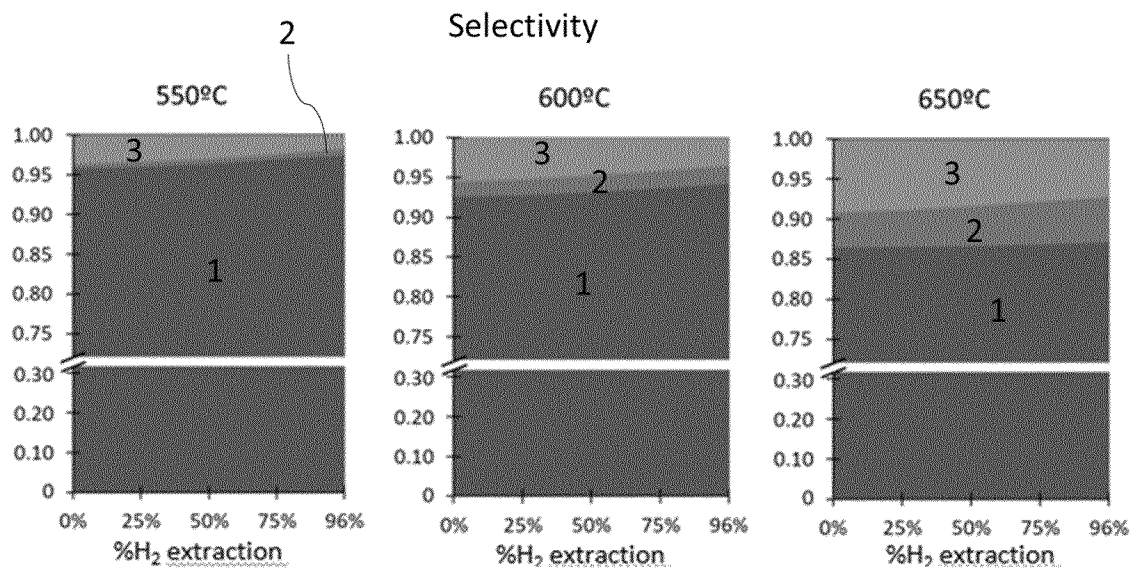


Fig. 16



1: propylene
 2: coke
 3: cracking products (ethane and methane)

Fig. 17

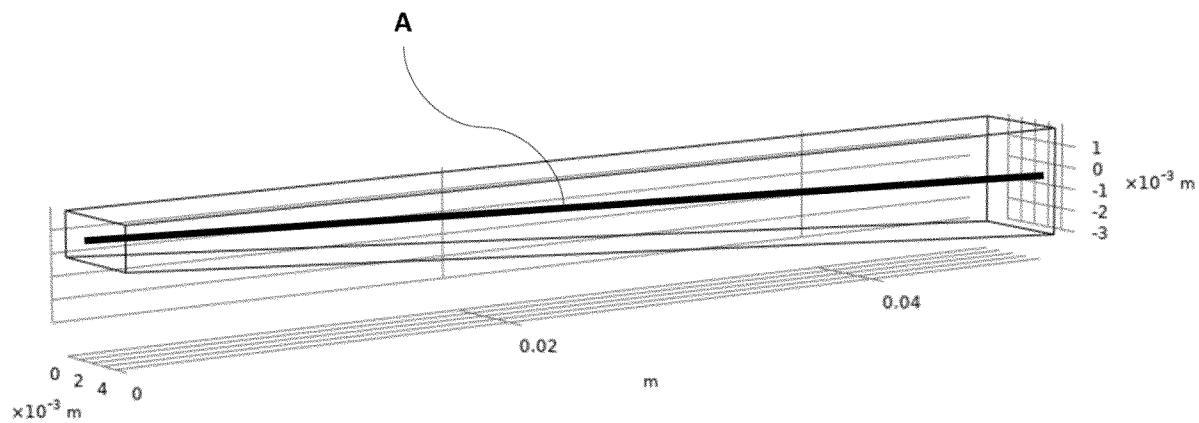


Fig. 18

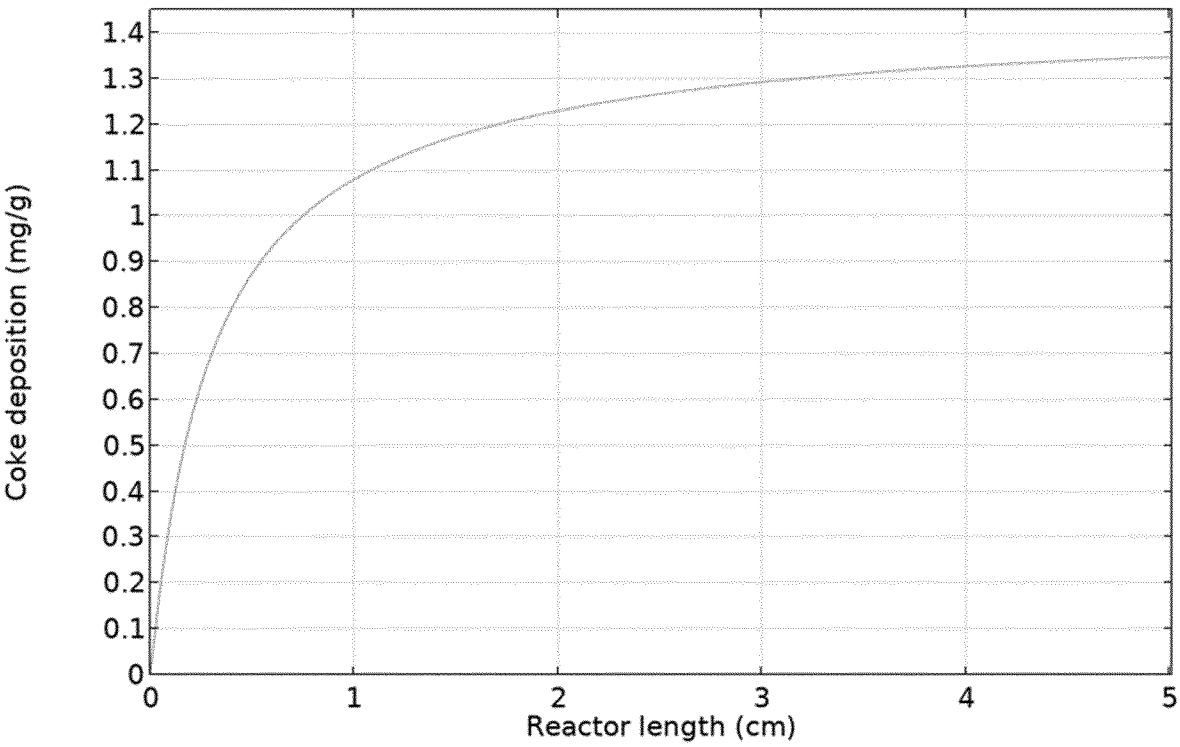


Fig .19

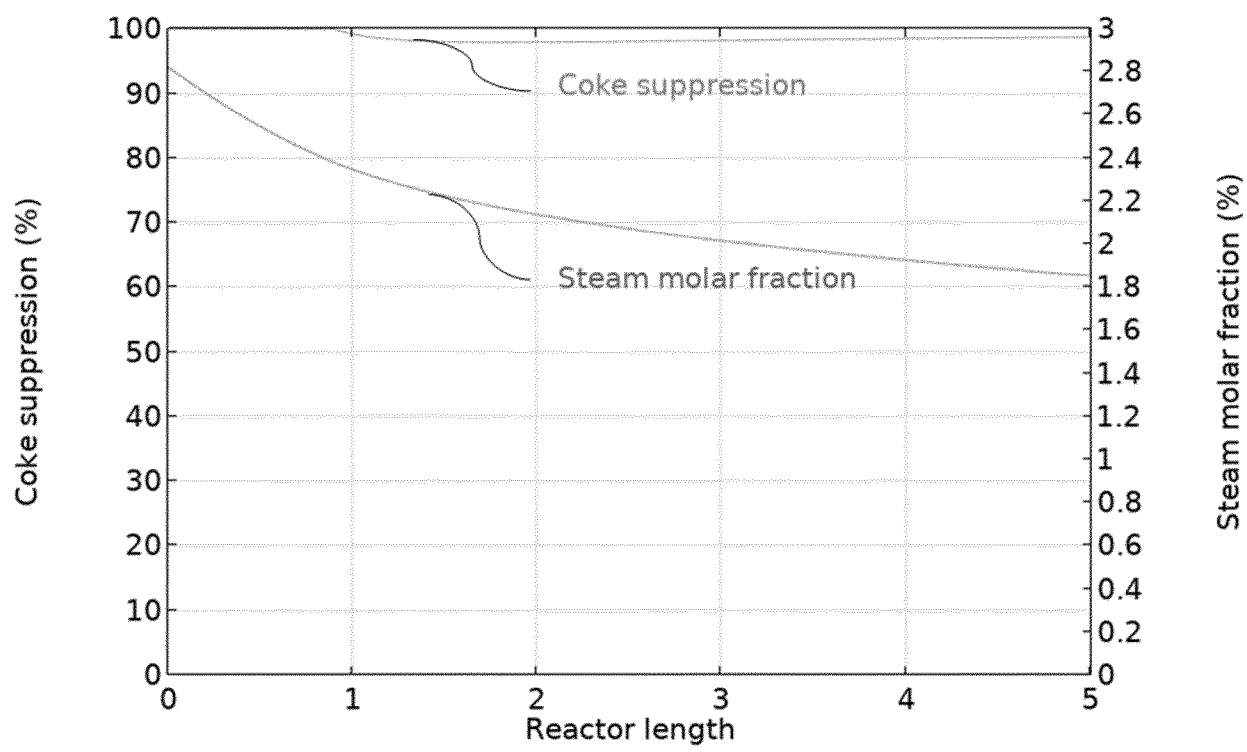


Fig. 20

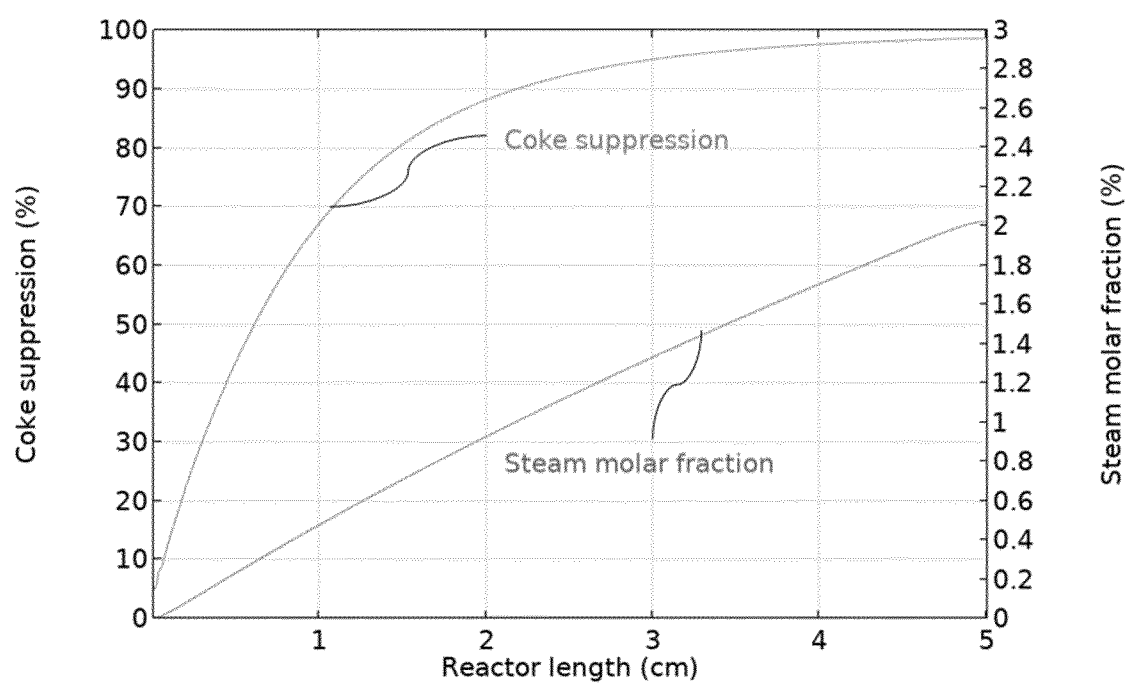


Fig. 21

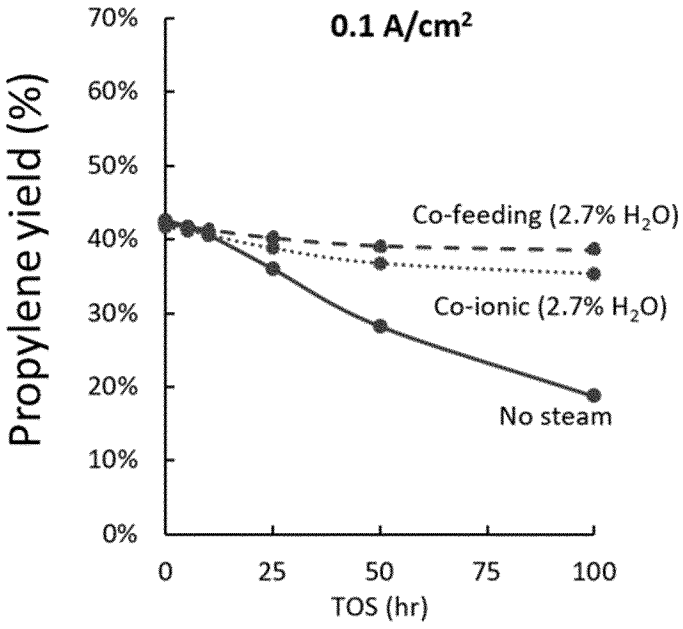


Fig. 22

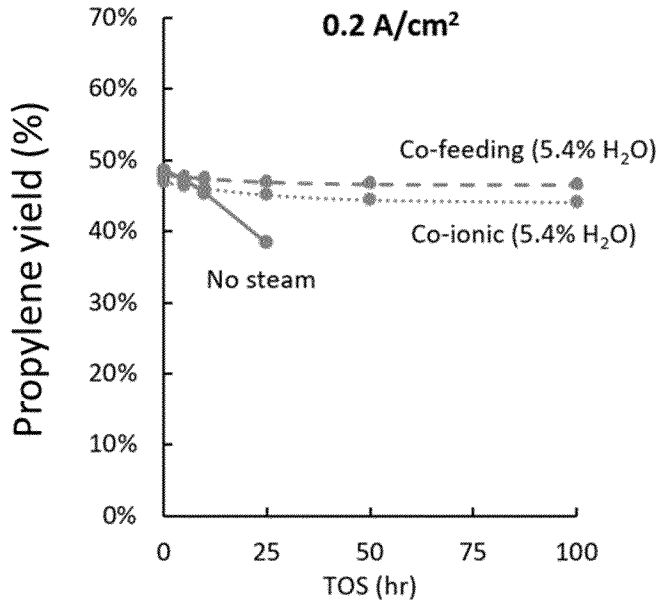


Fig. 23

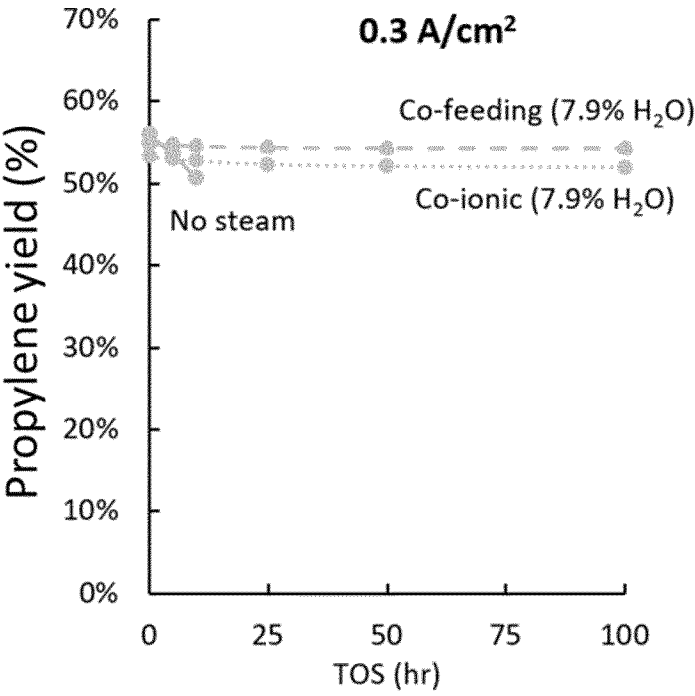


Fig. 24

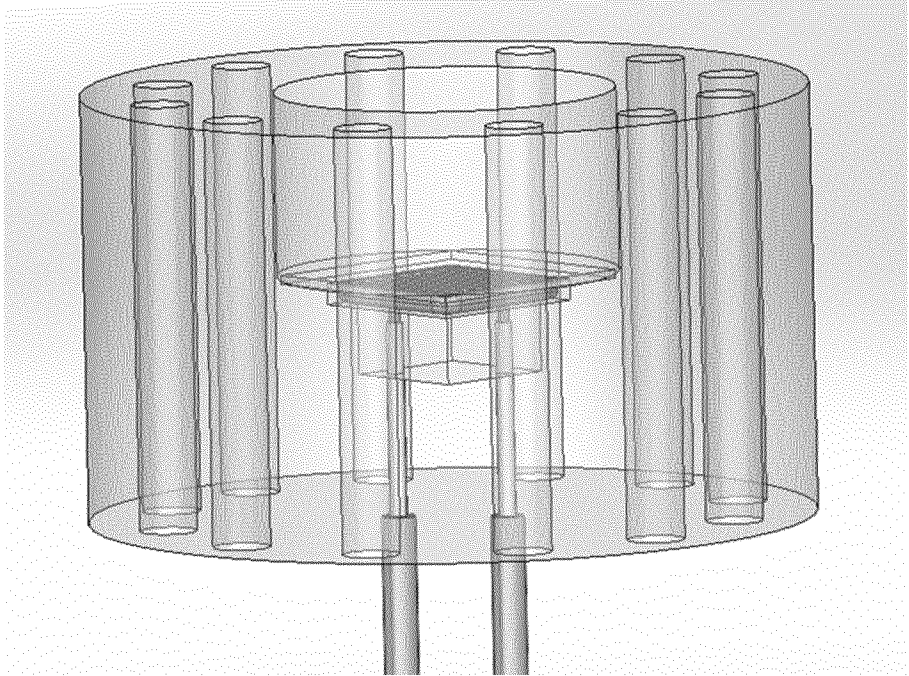


Fig. 25

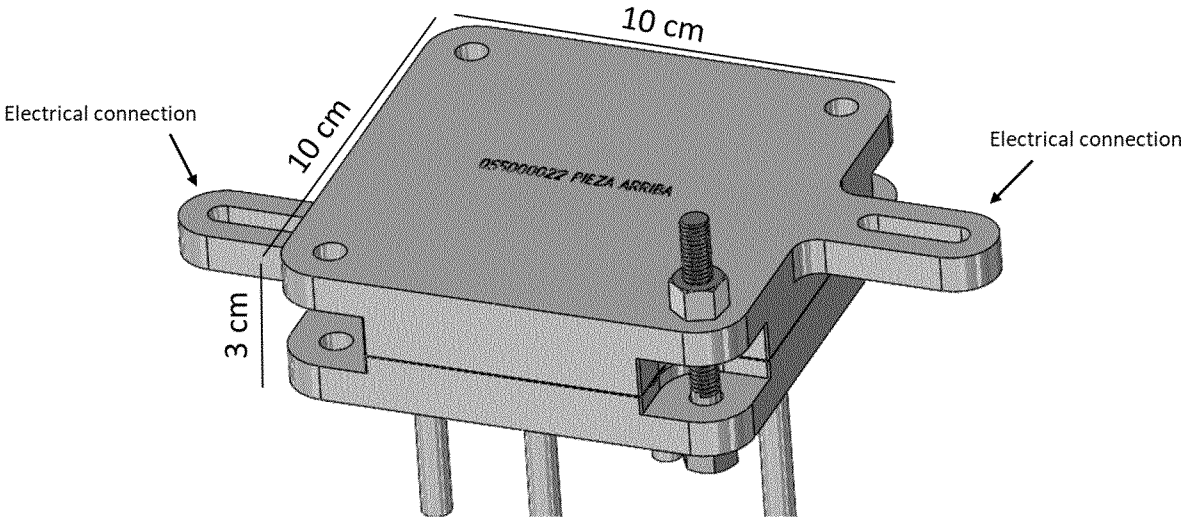


Fig. 26

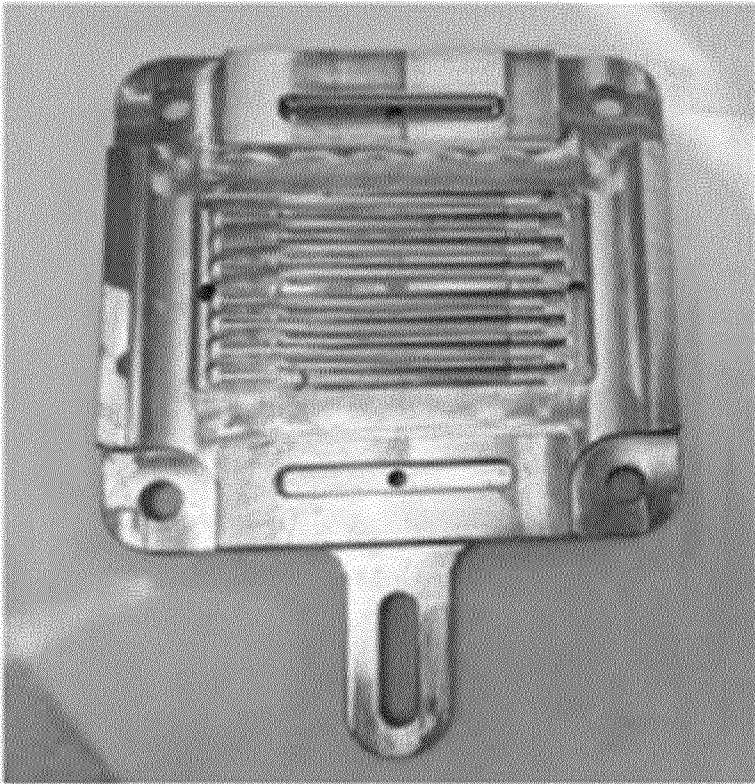


Fig. 27

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/066430

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	B01D69/14	B01D71/02	H01M4/90	C25B1/02	C25B3/03
	C25B3/23	C25B9/23	C25B11/073	C25B13/07	C25B15/08
ADD.					
According to International Patent Classification (IPC) or to both national classification and IPC					
B. FIELDS SEARCHED					
Minimum documentation searched (classification system followed by classification symbols)					
B01D H01M C25B					
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched					
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)					
EPO-Internal					
C. DOCUMENTS CONSIDERED TO BE RELEVANT					
Category*	Citation of document, with indication, where appropriate, of the relevant passages				Relevant to claim No.
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A	US 10 112 152 B2 (PROTIA AS [NO]) 30 October 2018 (2018-10-30) page 1				1 - 30

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A	DE 100 55 610 A1 (CREAVIS TECH & INNOVATION GMBH [DE]) 23 May 2002 (2002-05-23) page 1				1 - 30

☐ Further documents are listed in the continuation of Box C.					
☒ See patent family annex.					
* Special categories of cited documents :					
"A" document defining the general state of the art which is not considered to be of particular relevance			"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention		
"E" earlier application or patent but published on or after the international filing date			"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone		
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)			"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art		
"O" document referring to an oral disclosure, use, exhibition or other means			"&" document member of the same patent family		
"P" document published prior to the international filing date but later than the priority date claimed					
Date of the actual completion of the international search			Date of mailing of the international search report		
8 August 2024			20/08/2024		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016			Authorized officer Hoyer, Michael		

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2024/066430

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