



(51) International Patent Classification:

B01D 69/12 (2006.01) *B01D* 53/22 (2006.01)
B01D 71/02 (2006.01) *C01B* 3/50 (2006.01)

(21) International Application Number:

PCT/KR2014/007446

(22) International Filing Date:

11 August 2014 (11.08.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

10-2013-0094998 9 August 2013 (09.08.2013) KR

(71) Applicant: SAMSUNG ELECTRONICS CO., LTD.

[KR/KR]; 129, Samsung-ro, Yeongtong-gu, Suwon-si, Gyeonggi-do 443-742 (KR).

(72) Inventors: PARK, Hyeon Cheol; 354-2303, Dongtanjungang-ro 171, Hwaseong-si, Gyeonggi-do 445-734 (KR).

KIM, Kwang Hee; 101, Naksungdaeyeok 3-gil, Gwanak-gu, Seoul 151-832 (KR). MOON, Kyoung-Seok; 242-3001, Dongtanjungang-ro 213, Hwaseong-si, Gyeonggi-do

445-790 (KR). LEE, Jae-Ho; 517-101, Jinsan-ro 90, Suji-gu, Yongin-si, Gyeonggi-do 448-785 (KR). CHO, Keun-woo; 501-202, Nongogae-ro, Namdong-gu, Incheon, Gyeonggi-do 405-300 (KR). CHO, Eun Seog; 2403-903, Dongbaek 8-ro 90, Giheung-gu, Yongin-si, Gyeonggi-do 446-720 (KR).

(74) Agent: PANKOREA PATENT AND LAW FIRM; 13F, 70 Nonhyeon-ro 85-gil, Gangnam-gu, Seoul 135-933 (KR).

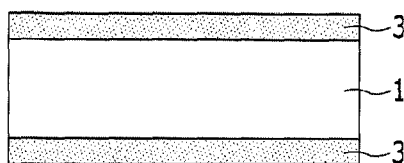
(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

[Continued on next page]

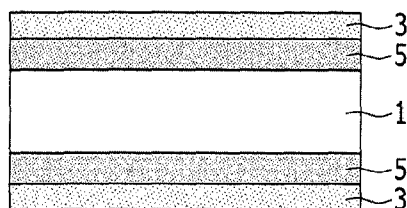
(54) Title: SEPARATION MEMBRANE, HYDROGEN SEPARATION MEMBRANE INCLUDING SEPARATION MEMBRANE, AND DEVICE INCLUDING HYDROGEN SEPARATION MEMBRANE

【Figure 1】

(a)



(b)



(57) Abstract: Disclosed are a separation membrane including a metal layer including vanadium (V) as a Group 5-based metal, and a nitride layer formed by nitride-treating the surface of the separation membrane, and a metal catalyst layer having hydrogen dissociation capability and being formed on the nitride layer, a hydrogen separation membrane including the separation membrane, a hydrogen separation device including the hydrogen separation membrane, and a method of manufacturing the separation membrane.



(84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (*Art. 21(3)*)
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (*Rule 48.2(h)*)

【DESCRIPTION】**【Invention Title】**

SEPARATION MEMBRANE, HYDROGEN SEPARATION MEMBRANE
INCLUDING SEPARATION MEMBRANE, AND DEVICE INCLUDING
5 HYDROGEN SEPARATION MEMBRANE

【Technical Field】

A separation membrane, a hydrogen separation membrane including the same, and a hydrogen separation device including the hydrogen separation membrane are disclosed.

10 **【Background Art】**

A hydrogen separation membrane selectively separating only hydrogen gas from a gas mixture including hydrogen gas is applied for separating, producing, and refining high purity hydrogen or the like. Most of the world's high purity hydrogen gas is generated using such a separation technology.
15 For example, when methane gas is modified, hydrogen (H₂) and carbon dioxide (CO₂) gasses are produced. By passing the mixed gas through the hydrogen separation membrane, high purity hydrogen may be obtained since carbon dioxide is not passed through the separation membrane, and only hydrogen gas is passed. As another example, there is a coal gasification reaction where
20 gases such as H₂ and CO₂ and the like are generated through coalification and a WGS (water gas shift) reaction, and only hydrogen gas is separated by passing through a separation membrane such that high purity hydrogen may be generated.

The separated hydrogen is used to generate electricity as a high purity energy source or to refine petroleum, or as a raw chemical material (NH₄, olefin, and the like). In addition, since the gas left after separating the hydrogen consists of CO₂ in a high concentration, the separation membrane may be used
5 to remove CO₂-rich gas through capture and storage.

As for a hydrogen separation membrane, a polymer, a ceramic, a metal, and the like have been developed, and in particular, a metal hydrogen separation membrane has very high purity hydrogen selectivity and may produce high purity hydrogen. In addition, the high purity hydrogen separated
10 from the metal hydrogen separation membrane may be directly used for a polymer electrolyte fuel cell and the like.

【Disclosure】

【Technical Problem】

One embodiment provides a novel separation membrane including a
15 Group 5-based metal, and having high hydrogen permeability and being capable of preventing it from diffusing into a noble metal catalyst layer or vice versa and thus preventing durability deterioration by nitride-treating the surface of the separation membrane.

Another embodiment of the present invention provides a method of
20 manufacturing the separation membrane.

Yet another embodiment of the present invention provides a hydrogen separation membrane including the separation membrane.

Yet another embodiment of the present invention provides a hydrogen

separation device including the hydrogen separation membrane.

【Technical Solution】

One embodiment provides a separation membrane including a Group 5-based metal, and a nitride layer formed by nitride-treating the surface of the separation membrane.

Specifically, the separation membrane may include a metal layer including vanadium (V) as the Group 5-based metal, a nitride layer of a metal forming the metal layer which is formed on at least one surface of the metal layer, and a metal catalyst layer having hydrogen dissociation capability which is formed on the nitride layer.

The metal layer may further include niobium (Nb), tantalum (Ta), or niobium and tantalum as the Group 5-based metal.

The separation membrane may include the nitride layer of the metal forming the metal layer which is formed by nitride-treating the surface of the metal layer.

The nitride layer of the metal may be a vanadium nitride layer, or a nitride layer of a V-Nb alloy, a nitride layer of a V-Ta alloy, or a nitride layer of a V-Nb-Ta alloy.

The nitride layer may be formed on at least one side of the separation membrane.

A thickness of the nitride layer may be less than or equal to about 50 nm, for example about 10 to about 40 nm.

The nitride-treating may be performed by treating the separation

membrane with nitrogen (N₂), or a mixed gas of nitrogen (N₂) and ammonia (NH₃).

The metal layer may further include an additional element belonging to any one of Groups 4, 8 to 10, and 14 of the periodic table as well as the Group

5 5-based metal, which are present as an alloy in the metal layer.

For example, the additional element belonging to Groups 4, 8 to 10, and 14 of the periodic table may be Ti, Zr, Hf, Fe, Ni, Ir, Pt, Ge, Si, or a combination thereof.

The separation membrane may have a body-centered cubic (BCC)
10 crystal structure due to the Group 5-based metal.

The metal catalyst layer having the hydrogen dissociation capability may include at least one metal selected from Pd, Pt, Ru, Ir, and a combination thereof, or an alloy of the foregoing metal, and at least one selected from Cu, Ag, Au, Rh, and a combination thereof.

15 According to another embodiment of the present invention, a hydrogen separation membrane including the separation membrane is provided.

The hydrogen separation membrane may have hydrogen solubility (H/M) of about 0.01 to about 0.6 measured under conditions of about a 0.1 to about 1 MPa hydrogen pressure and at about 400 °C.

20 The hydrogen separation membrane may have hydrogen solubility (H/M) of about 0.1 to about 0.5 measured under conditions of about 0.7 MPa (corresponding to about 7 bar) and at about 400 °C.

In one embodiment, the hydrogen separation membrane may have

hydrogen permeability of about 1.0×10^{-8} to about 15.0×10^{-8} mol/m*s*Pa^{1/2} at 400 °C.

According to yet another embodiment of the present invention, a hydrogen separation device including the hydrogen separation membrane is
5 provided.

The hydrogen separation device may further include a chamber equipped with a supplier for a mixed gas including hydrogen gas and a discharge chamber equipped with a discharger for separated hydrogen gas, wherein the hydrogen separation membrane contacts the chamber on one
10 surface of the hydrogen separation membrane and contacts the discharge chamber on the other surface.

In an exemplary embodiment, the hydrogen separation membrane may be formed in a tubular shape, a cylindrical chamber barrier rib having a larger diameter than that of the tubular hydrogen separation membrane may be
15 formed at the outside of the hydrogen separation membrane, a space between the chamber barrier rib and the hydrogen separation membrane may be formed as a chamber, and the inside of the tubular hydrogen separation membrane may be formed as a discharge chamber where hydrogen is discharged.

According to still another embodiment of the present invention, a
20 method of manufacturing the separation membrane is provided.

The method of manufacturing the separation membrane includes heat treating the surface of the metal layer including vanadium (V) as the Group 5-based metal with nitrogen (N₂) or a mixed gas of nitrogen (N₂) and ammonia (NH₃).

The heat-treating may be performed at a temperature of about 400 °C to about 1100 °C.

The method of manufacturing the separation membrane may further include coating the surface of the nitride layer formed by the heat-treating with a noble metal catalyst layer.

【Advantageous Effects】

Durability of a separation membrane can be improved by suppressing the formation of an intermetallic phase due to mutual diffusion between a metallic layer and a catalyst layer.

10 【Description of Drawings】

FIG. 1 schematically shows the cross-section of a hydrogen separation membrane including a catalyst layer 3 on a conventional metal layer 1 (FIG. 1 (a)) and the cross-section of a hydrogen separation membrane including a catalyst layer 3 having hydrogen dissociation capability on a nitride layer 5 after forming the nitride layer 5 on a metal layer 1 according to one embodiment of the present invention (FIG. 1 (b)).

FIG. 2 is a SEM photograph showing the cross-section of a hydrogen separation membrane including a nitride layer (VN) of a vanadium alloy by nitride-treating the surface of a vanadium-based alloy (V-Pt) according to one embodiment.

FIG. 3 is an EDX (energy dispersive x-ray analysis) graph respectively showing components of a nitride layer (VN) (c) and a vanadium alloy (V-Pt) metal layer (b) in the separation membrane (a) shown in FIG. 2.

FIG. 4 is a graph showing component analysis of a V-Ir alloy layer and a Pd catalyst layer formed thereon in a thickness direction through SIMS (secondary ion mass spectroscopy), and specifically, FIG. 4 (a) is a graph showing components of the layer before heat treatment, FIG. 4 (b) is a graph showing components of the layer in a thickness direction after heat treatment at 400 °C for 48 hours, and FIG. 4 (c) is a graph showing components of the separation membrane obtained by heat-retreating the Pd-coated separation membrane at 400 °C for 48 hours after nitride-treating a V-Ir alloy layer.

FIG. 5 is a schematic view showing a hydrogen separation device according to another embodiment.

FIG. 6 is a schematic view showing a hydrogen separation device including a tubular shape separation membrane according to another embodiment.

【Best Mode】

This disclosure will be described more fully hereinafter in the following detailed description, in which some but not all embodiments of this disclosure are described. However, this disclosure may be embodied in many different forms, and is not construed as limited to the exemplary embodiments set forth herein.

As those skilled in the art would realize, the described embodiments may be modified in various different ways, all without departing from the spirit or scope of this disclosure. The size and thickness of each constituent element as shown in the drawings are randomly indicated for better understanding and ease of description, and this disclosure is not necessarily limited to as shown.

The size and thickness of each constituent element as shown in the drawings are exaggeratedly indicated for better understanding and ease of description, and this disclosure is not necessarily limited to as shown.

According to one embodiment of the present invention, a separation
5 membrane including a Group 5-based metal and a nitride layer formed by
nitride-treating the surface of the separation membrane is provided.
Specifically, the separation membrane includes a metal layer including
vanadium (V) as the Group 5-based metal, a nitride layer of a metal forming the
metal layer, which is formed on at least one surface of the metal layer, and a
10 metal catalyst layer having hydrogen dissociation capability, which is formed on
the nitride layer.

The metal layer may further include niobium (Nb), tantalum (Ta), or
niobium and tantalum, which are Group 5 metals.

Therefore, the separation membrane may include a vanadium nitride
15 layer, or a nitride layer of a V-Nb alloy, a nitride layer of a V-Ta alloy, or a nitride
layer of a V-Nb-Ta alloy formed by nitride-treating the surface of the separation
membrane.

As the metal hydrogen separation membrane selectively separating only
hydrogen from the gas mixture including hydrogen, a palladium (Pd)-based
20 alloy has been widely researched. The Pd-based alloy acts as a catalyst in a
reaction in which hydrogen molecules are dissociated into hydrogen atoms from
the surface, and the hydrogen atoms may dissolve and diffuse through
interstices of unit cells due to a face-centered cubic (FCC) crystal structure and
are thus selectively separated (O. Hatlevik et al., J. of Separation and

Purification Technology, 73, 59-64, 2010).

However, the high price of the noble metal Pd is a limiting factor of commercializing a metal hydrogen separation membrane (in 2012, \$585/oz), and the development of an economical material for a hydrogen separation
5 membrane for substituting for Pd is urgently needed. Recently, a material using Group 5 elements such as vanadium (V), niobium (Nb), and tantalum (Ta) has been researched as the Pd substitute material.

Group 5 elements have a body-centered cubic (BCC) crystal structure, and thus Group 5-based metals have higher hydrogen permeation performance
10 of about 10 times to about 100 times that of pure Pd having a face centered cubic (FCC) crystalline structure. However, since the Group 5-based metals have no catalyst characteristics for the reaction of dissociating hydrogen molecules into hydrogen atoms, differing from Pd, the Group 5-based metals may permeate hydrogen by coating Pd on the surface thereof at a thickness of
15 several hundred nanometers.

On the other hand, the Pd and Group 5-based metal may form an intermetallic phase through mutual diffusion at a high temperature, and may cause durability deterioration. Accordingly, in this disclosure, a separation membrane includes a Group 5-based metal as a main component, and a nitride
20 layer of the metal formed on the surface thereof as a diffusion barrier layer to prevent mutual diffusion with a Pd-based catalyst layer, in order to solve the problems.

A separation membrane according to the embodiment includes a vanadium nitride layer, or a nitride layer of a V-Nb alloy, a nitride layer of a V-Ta

alloy, or a nitride layer of a V-Nb-Ta alloy on the surface thereof by nitride-treating the surface of the separation membrane including a Group 5-based metal, specifically V (vanadium), and additionally Nb, Ta, or a combination thereof.

5 The nitride layer may be formed on at least one side of the separation membrane, or both sides of the separation membrane.

 The nitride layer is formed in a thickness of less than or equal to about 50 nm, for example about 10 to about 40 nm, on the separation membrane, and the separation membrane including an additionally stacked metal catalyst layer
10 having hydrogen dissociation capability on the nitride layer may have sufficient hydrogen permeability of about $4 \times 10^{-8} \text{ mol/m}^2\text{sPa}^{1/2}$.

 However, if the nitride layer has a thickness of more than about 50 nm, hydrogen is not permeated well.

 The nitride-treating may be performed by treating the separation
15 membrane with nitrogen (N_2) or a mixed gas of nitrogen (N_2) and ammonia (NH_3). For example, while N_2 and NH_3 gases flow at each rate of about 200 sccm and about 50 sccm, and heat-treating is performed at a high temperature, for example about 400 to about 1100 °C, a nitride layer is formed on the surface of the separation membrane.

20 The metal layer may further include an additional element belonging to any one of Groups 4, 8 to 10, and 14 of the periodic table as well as the Group 5-based metal, which may be present as an alloy in the metal layer.

 For example, the additional element belonging to any one of Groups 4, 8 to 10, and 14 of the periodic table may be Ti, Zr, Hf, Fe, Ni, Ir, Pt, Ge, Si, or a

combination thereof.

When the separation membrane includes the additional metal as well as the Group 5-based metal, the nitride layer may include the additional metal.

The separation membrane has a body-centered cubic (BCC) crystal structure due to the Group 5 element, and accordingly a hydrogen atom that passes through the nitride layer may diffuse and permeate through interstices between unit cells of a BCC crystal structure of the metal layer including the Group 5 element.

The metal catalyst layer may include at least one selected from Pd, Pt, Ru, Ir, and a combination thereof, or an alloy of the foregoing metal, and at least one selected from Cu, Ag, Au, Rh, and a combination thereof.

Although the separation membrane includes the metal catalyst layer, the nitride layer prevents mutual diffusion between the metal catalyst layer and the Group 5-based metal layer, and durability deterioration does not occur after operation at a high temperature.

Another embodiment of the present invention provides a hydrogen separation membrane including the separation membrane.

The hydrogen separation membrane may have hydrogen solubility (H/M) of about 0.01 to about 0.6 measured under conditions of about a 0.1 MPa to about 1 MPa hydrogen pressure and at about 400 °C.

The hydrogen separation membrane may have hydrogen solubility (H/M) of about 0.1 to about 0.5 measured under conditions of about 0.7 MPa (corresponding to about 7 bar) and at about 400 °C.

In one embodiment, the hydrogen separation membrane may have

hydrogen permeability of about 1.0×10^{-8} to about 15.0×10^{-8} mol/m*s*Pa^{1/2} at about 400 °C.

According to another embodiment, a hydrogen separation device including the hydrogen separation membrane is provided.

5 The hydrogen separation device may include a chamber equipped with a supplier for a mixed gas including hydrogen gas and a discharge chamber equipped with a discharger for separated hydrogen gas, wherein the hydrogen separation membrane contacts the chamber on one surface of the hydrogen separation membrane, and contacts the discharge chamber on the other
10 surface.

FIG. 5 is a schematic view showing a hydrogen separation device 20 according to one embodiment. If a mixed gas including hydrogen gas is introduced into a chamber 22 through a supplier 21, only the hydrogen gas of the mixed gas is selectively separated into a discharge chamber 24 through the
15 hydrogen separation membrane 23. The separated hydrogen gas may be recovered through a discharger 25. The hydrogen separation device 20 may further include a recovery unit 26 for recovering a residual gas in the chamber 22, after the hydrogen is separated from the chamber 22. The hydrogen separation device 20 is shown in a simplified form for better comprehension and
20 easier description, and may further include additional constitutional components according to its use.

According to one embodiment, the hydrogen separation membrane may be formed in a tubular shape and may be formed with a cylindrical chamber barrier rib having a larger diameter of the tubular shaped hydrogen separation

membrane at the outside of the hydrogen separation membrane, wherein the space between the chamber barrier rib and the hydrogen separation membrane is formed as a space, and the inside of the tubular shaped hydrogen separation membrane may be formed as a chamber for discharging hydrogen.

5 FIG. 6 is a schematic view showing a tubular shaped hydrogen separation device 30 according to another embodiment. The hydrogen separation device 30 may include a tubular shaped hydrogen separation membrane 33, and a cylindrical chamber barrier rib 36 with a larger diameter than that of the tubular shaped hydrogen separation membrane and that is
10 formed on the outside of the hydrogen separation membrane 33. In this case, a space between the chamber barrier rib 36 and the hydrogen separation membrane 33 may be formed as a chamber 32, and a discharge chamber 34 for discharging hydrogen is formed inside the tubular shaped hydrogen separation membrane. The chamber 32 may be equipped with a supplier (not
15 shown) of a mixed gas including hydrogen gas, and a recovery unit (not shown) for recovering residual gas after the hydrogen gas is separated. Further, the discharge chamber 34 may be equipped with a discharger (not shown) for the separated hydrogen gas.

 According to another embodiment, a method of manufacturing the
20 separation membrane is provided.

 The method of manufacturing the separation membrane includes heat treating the surface of the metal layer including vanadium (V) as the Group 5-based metal with nitrogen (N_2), or a mixed gas of nitrogen (N_2) and ammonia (NH_3).

The heat-treating may be performed at a temperature of about 400 °C to about 1100 °C.

The method of manufacturing the separation membrane may further include coating the surface of the nitride layer formed by the heat-treating with a noble metal catalyst layer.

The metal catalyst layer is the same as described above and therefore a detailed description thereof is omitted.

Hereinafter, the embodiments are illustrated in more detail with reference to examples. However, they are exemplary examples of the present invention, and this disclosure is not limited thereto.

【Mode for Invention】

Example 1: Manufacture of Separation Membrane on which a Surface Nitride Layer is Formed, and Evaluation Thereof

A surface nitride layer is formed by heat-treating a V-Pt or V-Ir alloy layer for a predetermined time at a high temperature (400-1100 °C), while a gas ($\text{N}_2:\text{NH}_3 = 200 \text{ sccm}:50 \text{ sccm}$) flows therein. The nitride reaction temperature is controlled so that the nitride layer may have a thickness of 30-40 nm (650 °C, 5 min), 50-100 nm (850 °C, 5 min), and 200-500 nm (1000 °C, 5 min).

FIG. 2 is a SEM image showing the cross-section of the nitride layer on the V-Pt alloy surface. In addition, FIG. 3 is a graph showing component analysis of the nitride layer (VN) and the V-Pt alloy layer in FIG. 2. As shown from FIG. 3, nitrogen (N) element is found in the nitride layer (VN) (c), while no nitrogen (N) element is found in the V-Pt alloy layer (b).

On the other hand, each nitride layer having a different thickness is

formed, a Pd layer as a catalyst layer is deposited thereon to be 150 nm to 200 nm thick using a sputtering method, hydrogen pressure is applied at up to 7 bars in the feeding part of the separation membrane, hydrogen permeability of the separation membrane is measured according to the following Equation 1, and the results are provided in the following Table 1.

(Table 1)

Nitride Layer Thickness	Hydrogen Permeability
200 - 500 nm	Not permeated
50 - 100 nm	Not permeated
30 - 40 nm	$4 \times 10^{-8} \text{ mol/m}^2\text{sPa}^{1/2}$

The hydrogen permeability may be calculated according to the following Equation 1.

[Equation 1]

$$\text{Permeability} = (J \times L) / (\sqrt{P_{H_2, \text{in}}} - \sqrt{P_{H_2, \text{out}}})$$

10

In Equation 1, J is flux, L is a thickness of a separation membrane, $P_{H_2, \text{in}}$ is hydrogen feeding pressure, and $P_{H_2, \text{out}}$ is hydrogen permeation pressure.

Based on the results of Table 1, the nitride layer is required to have a thickness of less than or equal to 50 nm. When the nitride layer has a thickness ranging from 10 to 40 nm, efficient hydrogen permeability is obtained.

15

On the other hand, mutual diffusions of a separation membrane having the nitride layer and another separation membrane having no nitride layer are examined at a high temperature by measuring concentration of V, Pd, and Ir elements in a thickness direction before and after heat treatment of the

separation membrane including a Pd coating layer on a V-Ir separation membrane having no nitride layer and concentrations of V, Pd, Ir, and VN elements in a thickness direction in another separation membrane having a 30 - 40 nm thick nitride layer through SIMS (secondary ion mass spectroscopy) analysis, and the results are respectively provided in FIGS. 4A, 4B, and 4C.

As shown from FIG. 4A, when the separation membrane is coated with a Pd catalyst layer without forming a nitride layer on the surface, each element shows a sharply changed concentration on the interface between the two layers before the heat treatment, and as shown in FIG. 4B, the Ir, Pd, and V elements are spread on the interface of the two layers when the separation membrane is heat-treated at 400 °C for 48 hours.

On the other hand, the separation membrane having the nitride layer shows no diffusion between the metal layer and Pd, although the nitride layer has a small amount of Pd, as shown in FIG. 4C. The small amount of Pd is observed during the SIMS analysis, since a part of the elements in the Pd layer spreads inside the nitride layer when an ion beam is applied to the Pd layer from the top surface. In other words, the nitride layer prevents mutual diffusion of a metal of the vanadium (V) alloy layer and a metal of the metal catalyst layer (Pd).

Based on the results, a separation membrane preventing mutual diffusion between a Group 5-based metal and a catalyst layer at a high temperature and having excellent hydrogen permeability without durability deterioration is manufactured by nitride-treating the surface of the separation membrane including the Group 5-based metal to form a nitride layer.

While this disclosure has been described in connection with what is presently considered to be practical exemplary embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but, on the contrary, is intended to cover various modifications and equivalent
5 arrangements included within the spirit and scope of the appended claims.

【CLAIMS】**【Claim 1】**

A separation membrane, comprising:

a metal layer including vanadium (V) as a Group 5-based metal;

5 a nitride layer of the metal forming the metal layer, which is formed on at least one surface of the metal layer; and

a metal catalyst layer having hydrogen dissociation capability, which is formed on the nitride layer.

10 **【Claim 2】**

The separation membrane of claim 1, wherein the metal layer further comprises niobium (Nb), tantalum (Ta), or niobium and tantalum.

【Claim 3】

15 The separation membrane of claim 1, wherein the nitride layer has a thickness of less than or equal to about 50 nm.

【Claim 4】

The separation membrane of claim 1, wherein the nitride layer has a
20 thickness of about 10 to about 40 nm.

【Claim 5】

The separation membrane of claim 1, wherein the nitride layer is formed

by treating the surface of the metal layer with nitrogen (N₂) or a mixed gas of nitrogen (N₂) and ammonia (NH₃).

【Claim 6】

5 The separation membrane of claim 1, wherein the metal layer further comprises an additional element belonging to any one of Groups 4, 8 to 10, and 14 of the periodic table.

【Claim 7】

10 The separation membrane of claim 6, wherein the additional element belonging to any one of Groups 4, 8 to 10, and 14 of the periodic table is Fe, Ni, Ir, Pt, Ge, Si, or a combination thereof.

【Claim 8】

15 The separation membrane of claim 7, wherein the additional element belonging to any one of Groups 4, 8 to 10, and 14 of the periodic table is Ir or Pt.

【Claim 9】

20 The separation membrane of claim 1, wherein the metal layer of the separation membrane has a body-centered cubic (BCC) crystal structure.

【Claim 10】

 The separation membrane of claim 1, wherein the metal catalyst layer

comprises at least one metal selected from Pd, Pt, Ru, Ir, and a combination thereof, or an alloy of the foregoing metal and at least one selected from Cu, Ag, Au, Rh, and a combination thereof.

5 **【Claim 11】**

A hydrogen separation membrane comprising the separation membrane according to claim 1.

【Claim 12】

10 The hydrogen separation membrane of claim 11, wherein the hydrogen separation membrane has hydrogen solubility (H/M) of about 0.01 to about 0.6 measured under conditions of about 0.1 MPa to about 1 MPa of hydrogen pressure and at about 400 °C.

15 **【Claim 13】**

The hydrogen separation membrane of claim 11, wherein the hydrogen separation membrane has hydrogen solubility (H/M) of about 0.1 to about 0.5 measured under conditions of about 0.7 MPa (corresponding to about 7 bar) and at about 400 °C.

20

【Claim 14】

The hydrogen separation membrane of claim 11, wherein the hydrogen separation membrane has hydrogen permeability of about 1.0×10^{-8} to about

15.0×10⁻⁸ mol/m*s*Pa^{1/2} at 400 °C.

【Claim 15】

A hydrogen separation device comprising the hydrogen separation
5 membrane according to claim 11.

【Claim 16】

The hydrogen separation device of claim 15, further including a chamber
equipped with a supplier for a mixed gas including hydrogen gas, and
10 a discharge chamber equipped with a discharger for separated
hydrogen gas,

wherein the hydrogen separation membrane contacts the chamber on
one surface of the hydrogen separation membrane, and contacts the discharge
chamber on the other surface.

15

【Claim 17】

The hydrogen separation device of claim 16, wherein the hydrogen
separation membrane is formed in a tubular shape, a cylindrical chamber
barrier rib having a larger diameter than that of the tubular hydrogen separation
20 membrane is formed at the outside of the hydrogen separation membrane, a
space between the chamber barrier rib and the hydrogen separation membrane
is formed as a chamber, and the inside of the tubular hydrogen separation
membrane is formed as a discharge chamber where hydrogen is discharged.

【Claim 18】

A method of manufacturing a separation membrane, comprising heat
treating the surface of the metal layer including vanadium (V) as the Group 5-
5 based metal with nitrogen (N_2) or a mixed gas of nitrogen (N_2) and ammonia
(NH_3) to manufacture the separation membrane according to claim 1.

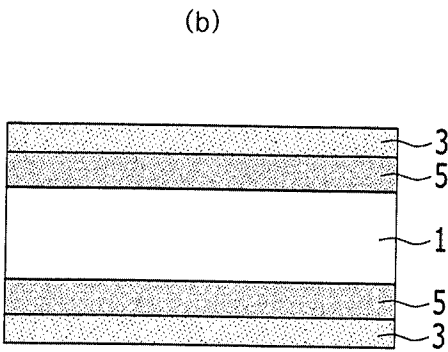
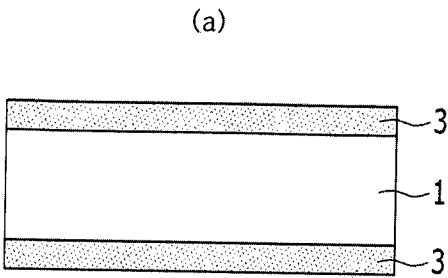
【Claim 19】

The method of claim 18, wherein the heat-treating is performed at a
10 temperature of about 400 °C to about 1100 °C.

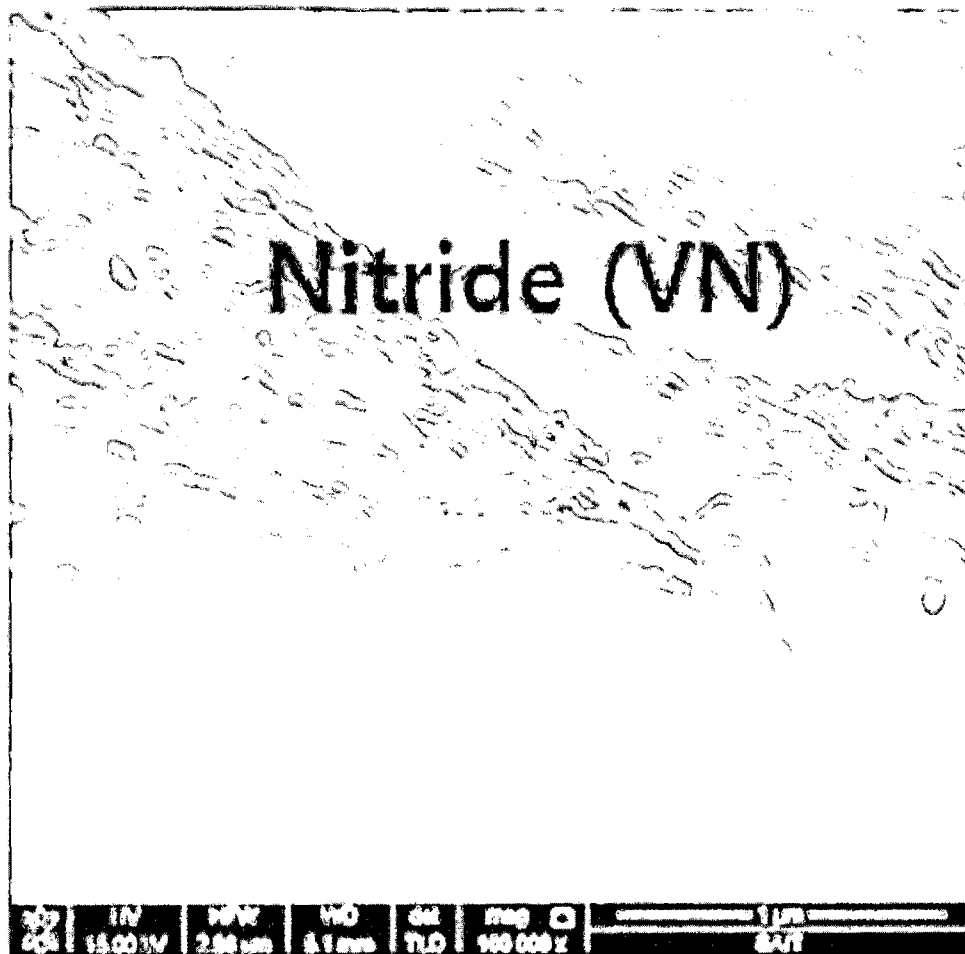
【Claim 20】

The method of claim 18, which further comprising coating the surface of
the nitride layer formed by the heat-treating with a noble metal catalyst layer
15 having hydrogen dissociation capability.

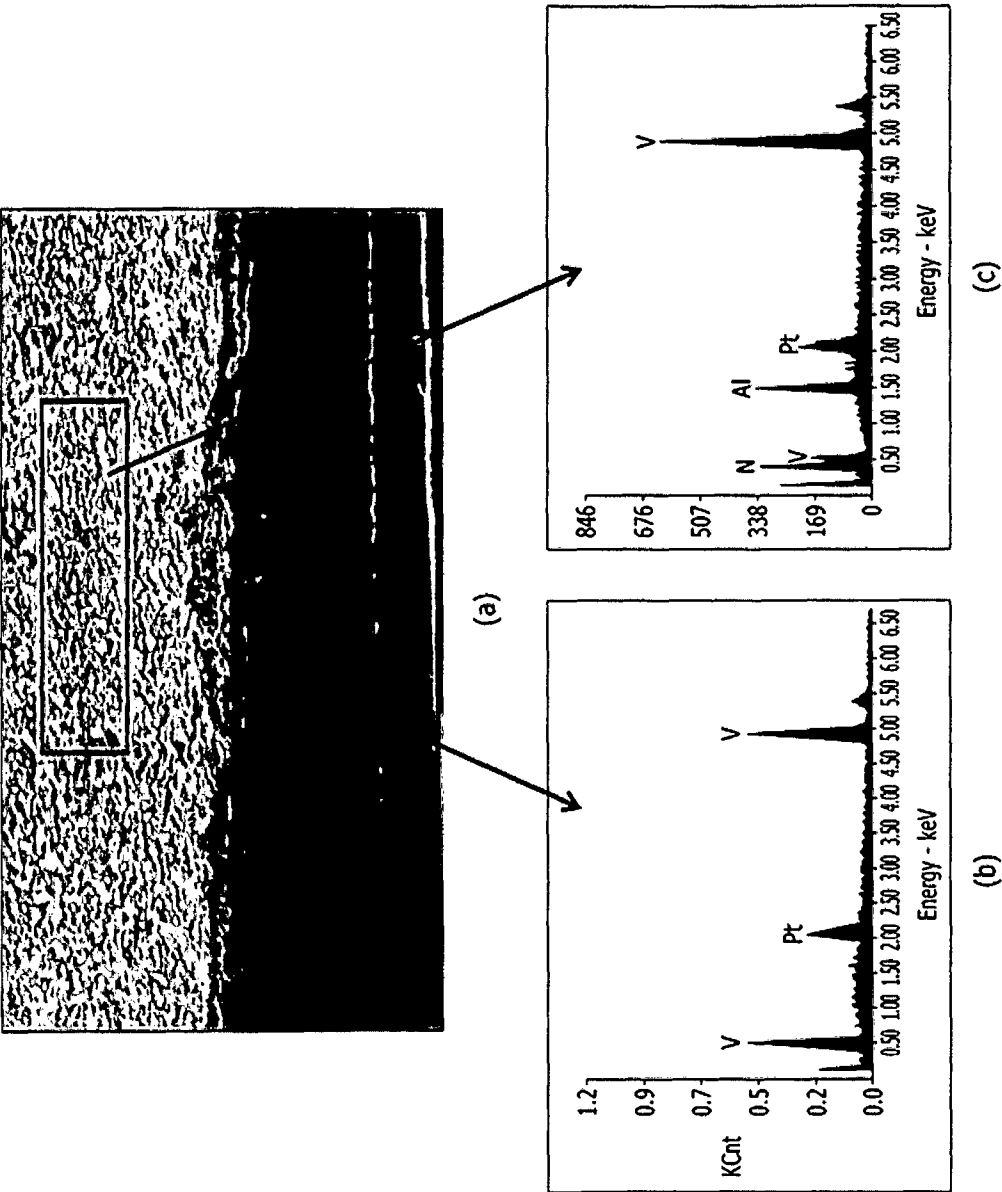
【Figure 1】



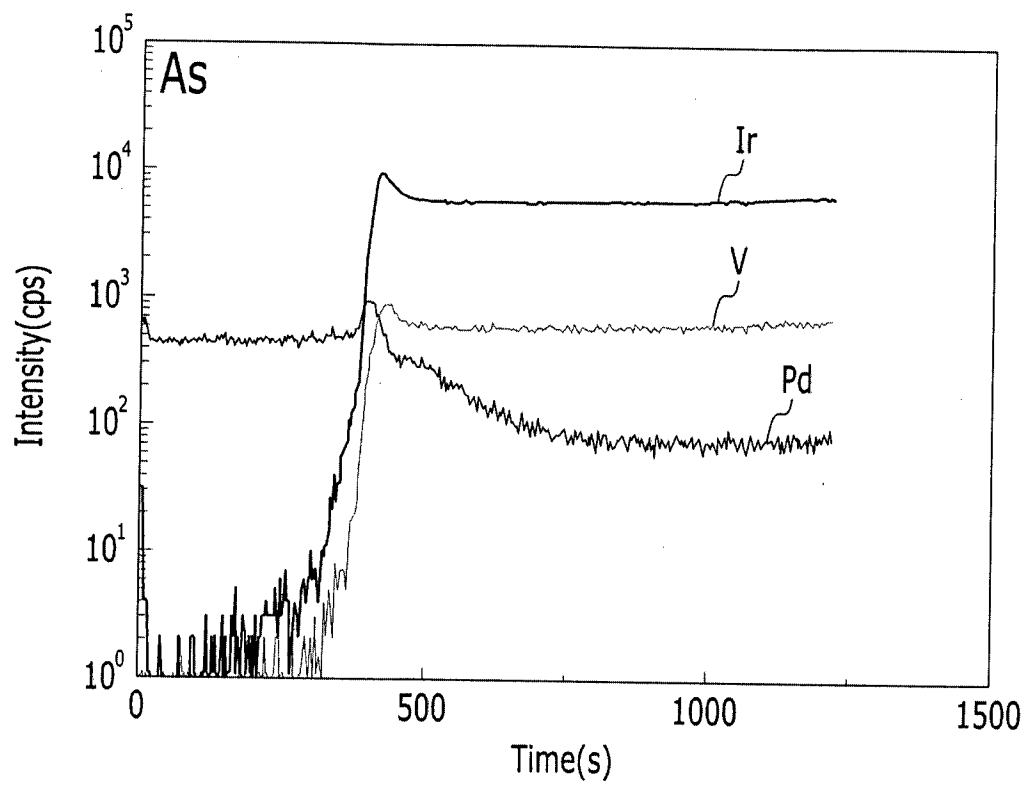
【Figure 2】



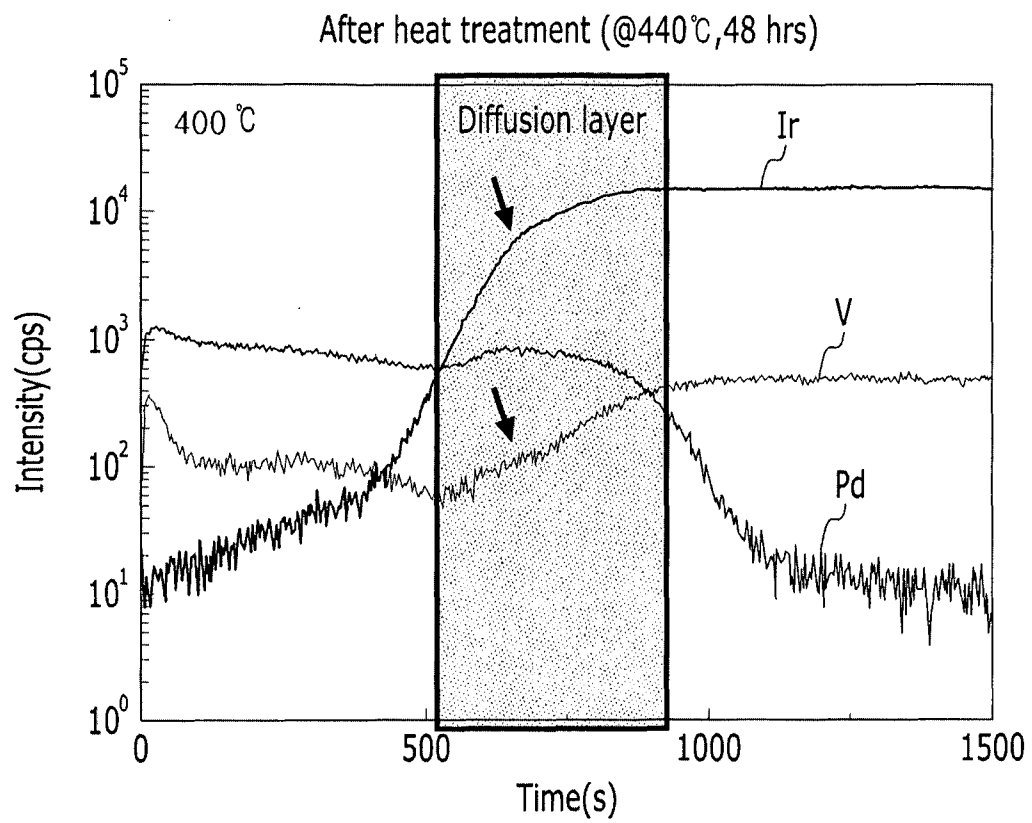
【Figure 3】



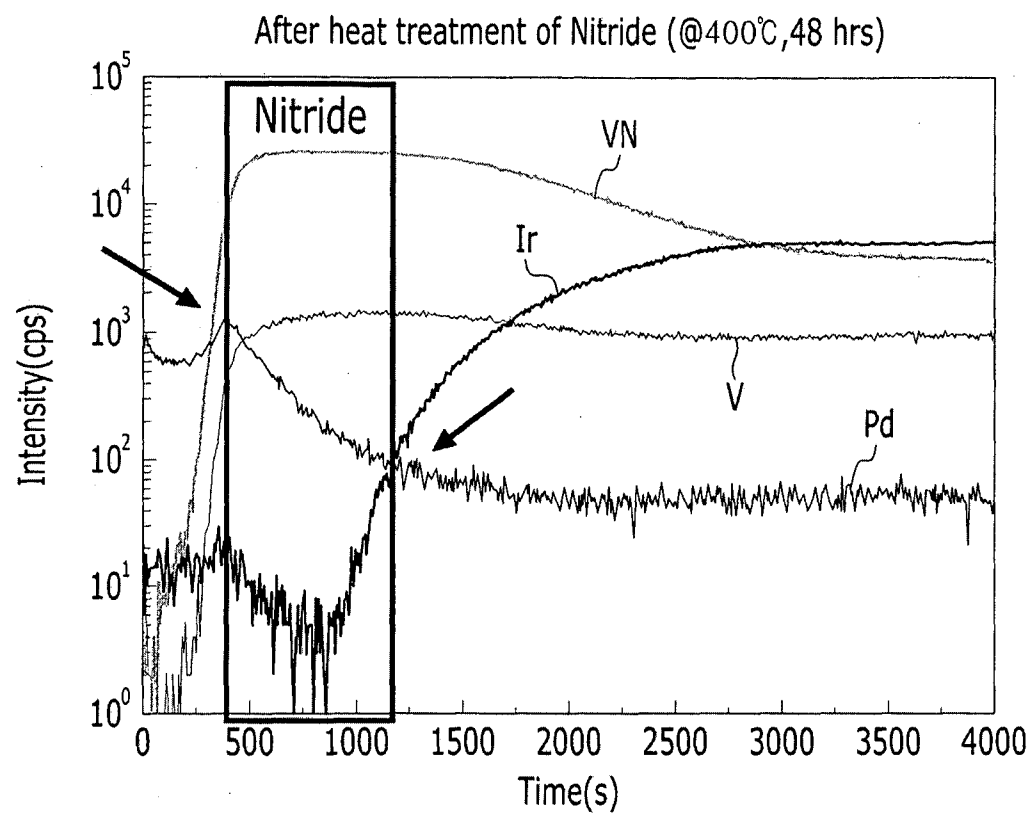
【Figure 4A】



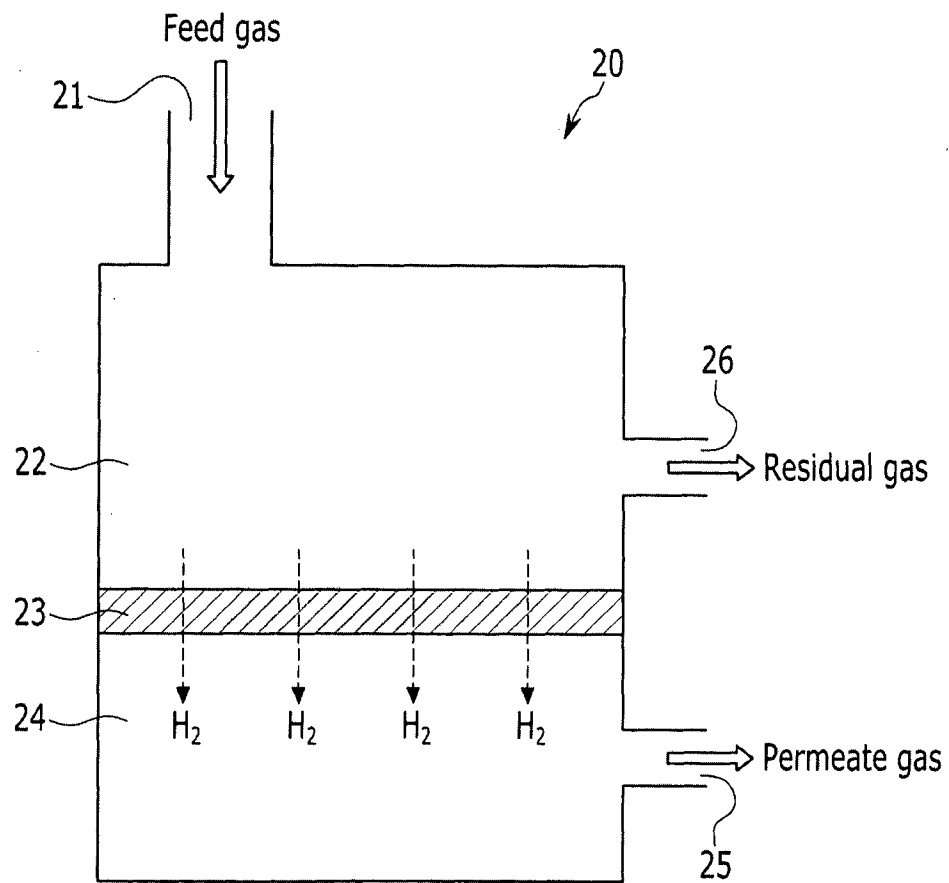
【Figure 4B】



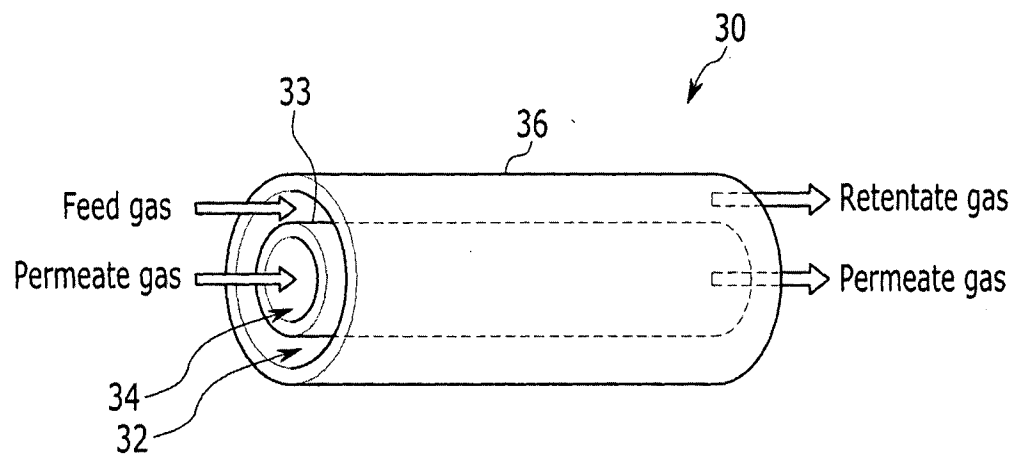
【Figure 4C】



【Figure 5】



【Figure 6】



A. CLASSIFICATION OF SUBJECT MATTER**B01D 69/12(2006.01)i, B01D 71/02(2006.01)i, B01D 53/22(2006.01)i, C01B 3/50(2006.01)i**

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 69/12; B01J 8/02; B01D 53/22; B01D 67/00; B01D 71/02; C01B 3/56; C01B 3/50

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: hydrogen separation, membrane, metal layer, Group 5-based metal, vanadium, nitride layer, metal catalyst layer**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2007-044622 A (TOYOTA MOTOR CORP.) 22 February 2007 See abstract; claims 1-4; paragraphs [0005]-[0007], [0041]-[0049], [0058]-[0064]; and figures 1, 4.	1-15, 18-20
Y		16, 17
Y	US 2013-0136666 A1 (PARK, H. C. et al.) 30 May 2013 See abstract; paragraphs [0032]-[0036], [0108]; and figures 13, 14.	16, 17
A	JP 2007-044593 A (TOYOTA MOTOR CORP.) 22 February 2007 See abstract; and claims 1, 2.	1-20
A	US 6152987 A (MA, Y. H. et al.) 28 November 2000 See abstract; claims 17-28; and columns 4, 5.	1-20
A	US 2003-0213365 A1 (JANTSCH, U. et al.) 20 November 2003 See abstract; claim 1; and paragraphs [0001], [0019], [0031]-[0033].	1-20



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

"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search

15 December 2014 (15.12.2014)

Date of mailing of the international search report

16 December 2014 (16.12.2014)

Name and mailing address of the ISA/KR

International Application Division
Korean Intellectual Property Office
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan City, 302-701,
Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

LEE, Dong Wook

Telephone No. +82-42-481-8163



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2014/007446

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2007-044622 A	22/02/2007	JP 4665656 B2	06/04/2011
US 2013-0136666 A1	30/05/2013	EP 2596851 A1	29/05/2013
		JP 2013-111576 A	10/06/2013
		KR 10-2013-0057931 A	03/06/2013
JP 2007-044593 A	22/02/2007	JP 4661444 B2	30/03/2011
US 06152987 A	28/11/2000	AU 1999-17251 A1	05/07/1999
		CA 2315029 A1	24/06/1999
		CA 2315029 C	09/12/2008
		EP 1042049 A1	11/10/2000
		EP 1042049 B1	19/03/2003
		WO 99-30806 A1	24/06/1999
US 2003-0213365 A1	20/11/2003	AT 375194 T	15/10/2007
		AU 2003-203623 A1	04/12/2003
		BR 0301586 A	24/08/2004
		BR 0301586 B1	08/02/2011
		CA 2423427 A1	17/11/2003
		CA 2423427 C	10/10/2006
		CN 1460539 A	10/12/2003
		CN 1460539 B	11/08/2010
		DE 10222568 A1	04/12/2003
		DE 10222568 B4	08/02/2007
		DE 50308332 D1	22/11/2007
		EP 1362630 A1	19/11/2003
		EP 1362630 B1	10/10/2007
		JP 2004-000970 A	08/01/2004
		KR 10-2003-0089421 A	21/11/2003
		US 6761755 B2	13/07/2004