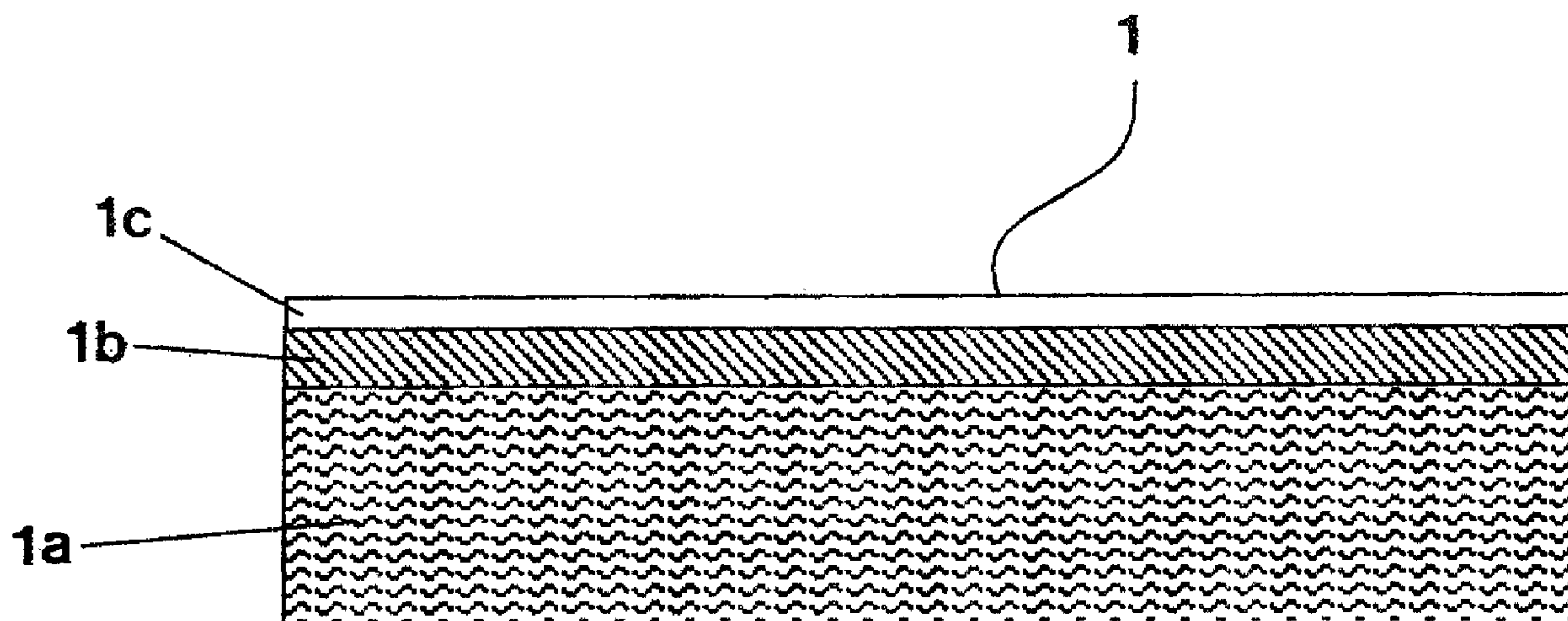




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(57) **Abrégé/Abstract:**

The invention relates to a composite membrane having a flexible metallic substrate for separation of hydrogen from gas mixtures, which achieves a separation ratio of hydrogen to nitrogen of greater than 4,000 at operating temperatures higher than 300°C, and also to a method for production of such a composite membrane.

## Abstract

The invention relates to a composite membrane having a flexible metallic substrate for separation of hydrogen from gas mixtures, which achieves a separation ratio of hydrogen to nitrogen of greater than 4,000 at operating temperatures higher than 300°C, and also to a method for production of such a composite membrane.

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## **Composite Membrane and Production Method Therefor**

### Specification

The invention relates to a composite membrane with a flexible, metallic substrate and a layer system arranged on at least one surface of the substrate; the layer system being formed of a rigid, non-self-supporting, nonmetallic inorganic diffusion barrier layer and at least one hydrogen-permeable, nonporous metallic membrane layer; and the diffusion barrier layer being arranged between the substrate and the at least one membrane layer and being formed by at least one single layer. The invention further relates to a method for the production of such a composite membrane.

Such membranes are known, for example, from EP 783 919 A1 or EP 718 031 A1. A composite membrane is disclosed there which has a support of hydrogen-permeable metal or hydrogen-permeable ceramic, wherein the support can be flexible as well as rigid. The support can be made porous, using a fabric of stainless steel. A porous, flexible diffusion barrier layer, which consists of a non-sintered material such as felt, paper or fiber mats, is situated on this support. It is further disclosed that a rigid diffusion barrier layer can also be used, if the hydrogen-permeable membrane layer arranged above it is textured. Oxides, sulfides, nitrides, carbides and silicides are disclosed as materials for a rigid diffusion barrier layer. It is indicated that these rigid diffusion barrier layers frequently have cracks. The hydrogen-permeable membrane layer arranged over the diffusion barrier layer is textured when a rigid diffusion barrier layer is used, while this is not absolutely required when a porous, flexible diffusion barrier layer is used. The membrane layer is formed from metals of Group VIIb or VIIIb, the metals Fe, Mn, Ni, Pd, Pt

and Ru being specifically mentioned here. The hydrogen-permeable membrane layer can be formed, for example, by electrodeposition on the porous, flexible diffusion barrier layer. The textured membrane layer required on the diffusion barrier layer is constituted as a self-supporting, shaped metal sheet for forming the composite membrane.

US 5,393,325 describes a composite membrane with a nonporous, hydrogen-permeable metal support, on which a non-metallic diffusion barrier layer is arranged. Disclosed therein as materials for the diffusion barrier layer are oxides, sulfides, carbides, nitrides or silicides. Aluminum oxide, lanthanum oxide, molybdenum oxide, silicon dioxide, tungsten oxide, yttrium oxide and vanadium sulfide are mentioned as preferred materials. A non-porous, hydrogen-permeable metallic layer of, for example, Pd, Pt, Fe, Ru, Ni or Mn is arranged on the diffusion barrier layer.

WO 99/33545 discloses a support structure of porous stainless steel, whose surface is sintered with a fine nickel powder. The thus pretreated surface is electroplated with copper and then provided with a further electroplated layer of a hydrogen-permeable metallic alloy as, e.g., a palladium alloy.

EP 0 348 041 B1 describes a composite membrane with an inorganic support of fibers, whose fiber interstices have a diameter  $> 5 \mu\text{m}$  and a length smaller than ten times the diameter. The inorganic support is coated with a porous inorganic film, which is made of non-metallic, sintered particles and has a pore size of up to  $2 \mu\text{m}$ . Glass, mineral, or metal fiber materials are disclosed here as the support materials. For the porous, inorganic film, there are proposed metal oxides, for example, titanium dioxide, aluminum oxide, cerium oxide, zirconium dioxide, mullite or mixtures thereof. It is mentioned that cracks can appear in the porous inorganic film due to bending of the membrane.

US 4,468,235 discloses a hydrogen-permeable membrane with a nonporous support made of a titanium alloy, which is coated with a metal or metallic alloy of

the group of palladium, nickel, cobalt, iron, vanadium, niobium or tantalum. This coating is produced on the support by electroplating or by sputtering.

WO 90/09231 describes a hydrogen-permeation membrane with an inorganic support having gaps, wherein the gaps are bridged over by a composite layer of nonmetallic particles and metal. Palladium is disclosed here as the metal.

JP 346824/92 and JP 76 738/93 disclose a hydrogen-permeable membrane made of palladium on a porous metallic support, wherein a ceramic barrier layer or a metal oxide barrier layer is arranged between the membrane and the metallic support.

US 5,259,870 describes a hydrogen-permeable composite membrane with a support made of nonporous metal, a diffusion barrier layer made of a metal oxide, and a membrane layer made of palladium or palladium alloy.

RU 1,058,587 discloses a hydrogen-permeable membrane with a metal support, which is bonded by diffusion welding to a layer of palladium or palladium alloy. Ultrafine metal oxide powder is arranged between the metal support and the layer of palladium or palladium alloy.

Further hydrogen-permeation membranes are known from US 4,496,373, US 5,094,927, US 2,958,391, US 3,477,288, US 4,699,637, US 4,388,479, US 3,622,303, US 3,350,846, US 1,174,631, US 2,773,561, US 3,393,098, and EP 0 242 208, and also the publications "Inorganic Membrane Reactors" (H.P. Hsieh, *Catal. Rev. - Sci. Eng.*, 33(1&2), 1-70, 1991), "Preparation and Characterization of a Composite Palladium-Ceramic Membrane" (P. Collins, *Ind. Eng. Chem. Res.*, Vol. 32, No. 12, 3006-3013, 1993) or "Hydrogen Diffusion Membranes based on some Palladium-Rare Earth Solid Solution Alloys" (D.T. Hughes and I.R. Harris, *Zeitschrift für physik. Chemie*, Vol. 117, pp. 185-193, 1979).

The problem is posed of providing an effective composite membrane for separating hydrogen from gas mixtures which attains a separation ratio of hydro-

gen to nitrogen of greater than 4,000 at operating temperatures of greater than 300°C.

The separation ratio is determined by separate determinations of the through-flow rates for pure nitrogen and pure hydrogen through the composite membrane, and gives the selectivity of the membrane. The respective volume flows of permeate through the composite membrane are measured. The ratio of the volume flows  $H_2/N_2$  is above all a measure of the imperviousness of the membrane or for the number of undesired pores and defective places in the membrane layer. For example, a  $H_2/N_2$  value  $< 500$  shows that the separating action of the membrane is small and the number of pores or defective places in the membrane layer is high.

The problem is solved in that at least the single layer of the diffusion barrier layer directly adjoining on the membrane layer is open-pored and/or has microcracks and on its surface facing away from the substrate has an electrical resistivity of less than 10  $\Omega\text{cm}$  at a temperature of 20°C, and wherein the substrate has an open porosity in a range of about 15% to 60% and the at least one membrane layer is electrodeposited on the surface of the at least one diffusion barrier layer facing away from the substrate. By a rigid diffusion barrier layer is understood a brittle, compact layer, firmly adherent to the substrate, which can consist of plural individual layers. Due to the surface of the diffusion barrier layer facing away from the substrate having a low resistivity of less than 10  $\Omega\text{cm}$ , a closed membrane layer can be electrodeposited on this surface. It is thus possible to use a multi-layer diffusion barrier layer, which can, for example, also contain electrically insulating single layers, as long as the single layer of the diffusion barrier layer directly adjoining the membrane layer has this low resistivity. If the diffusion barrier layer also has nonporous or crack-free individual layers, these must be formed of a hydrogen-permeable material.

The composite membrane according to the invention has a high permeability for hydrogen, such that a separation ratio of hydrogen to nitrogen of greater than

4,000 is attained. Although a rigid structure is concerned in the diffusion barrier layer, which can already have microcracks before the formation of the membrane layer, the finished composite membrane is, surprisingly, not unusable when it is slightly bent. The composite membrane according to the invention is furthermore insensitive to thermally induced mechanical stresses, such as may arise, for example, during a temperature change from room temperature to 400°C.

It is particularly preferred when the single layer of the diffusion barrier layer which is directly adjacent to the membrane layer has, on its surface facing away from the substrate, an electrical resistivity of less than 10,000  $\mu\Omega\text{cm}$  at a temperature of 20°C, particularly less than 1,000  $\mu\Omega\text{cm}$ . The membrane layer is thereby homogeneously deposited.

Stainless steel has been found to be suitable as the material for the flexible substrate.

The single layer of the diffusion barrier layer directly adjoining the membrane layer is preferably formed from a metal nitride. Here, the metal nitrides with at least one metal of the group of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten are particularly preferred. Metal nitrides have a low electrical resistivity and can be electroplated directly with the membrane layer. Titanium nitride has been found to be particularly suitable here. Besides the metals titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, the metal nitride can additionally contain aluminum.

Furthermore it has proved effective when the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed from a metal oxide. In particular, substoichiometric metal oxides are preferred here, which have an especially good electrical conductivity. A substoichiometric titanium oxide has proved to be particularly effective here. Furthermore, the noble metal oxides: ruthenium oxide ( $\text{RuO}$ ,  $\text{RuO}_2$  or  $\text{Ru}_2\text{O}_3$ ), or iridium oxide ( $\text{IrO}$ ,  $\text{IrO}_2$  or  $\text{Ir}_2\text{O}_3$ ) are pre-

ferred. The use of rhodium oxide ( $\text{RhO}$  or  $\text{Rh}_2\text{O}_3$ ) has also proved effective. These noble metal oxides have a low electrical resistivity, so that a direct application of the membrane layer by electroplating is possible.

It has furthermore proved effective to form the single layer of the diffusion barrier layer directly adjoining the membrane layer from a metal carbide. Here, metal carbides with at least one metal of the group of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten have proved effective. These metal carbides have a low electrical resistivity and can be directly electroplated with the membrane layer. Particularly preferred in this connection is tungsten carbide. The metal carbide can here contain included carbon, which does not impair its function.

It has furthermore proved effective when the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of a metal oxynitride. Here, a metal oxynitride is preferred with at least one metal from the group of titanium, zirconium and hafnium, which can be directly electroplated with the membrane layer. Titanium oxynitride is particularly preferred here. Besides the at least one metal of the group of titanium, zirconium and hafnium, the metal oxynitride may also contain aluminum.

Furthermore, it has proved effective if the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of a metal carbonitride. The metal carbonitrides which can be electroplated directly with the membrane layer, and which are formed with at least one metal of the group of vanadium, niobium, tantalum, chromium, molybdenum and tungsten, have proved particularly effective here. Titanium carbonitride is particularly preferred here. Niobium carbonitrides, such as  $\text{NbC}_{0.3}\text{N}_{0.7}$ , are also suitable.

Furthermore, it has proved effective when the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of a metal boride. Suitable metal borides which can be electroplated directly with the membrane layer

are, for example, formed with at least one metal of the group of niobium, titanium, zirconium, cerium and barium. Particularly preferred here are cerium hexaboride ( $\text{CeB}_6$ ), titanium diboride ( $\text{TiB}_2$ ), and also niobium boride ( $\text{NbB}$ ) or niobium diboride ( $\text{NbB}_2$ ).

The flexible metallic substrate is preferably formed of metal fibers, wherein the interstices between the metal fibers have a width and length, respectively, of  $< 5 \mu\text{m}$ , or the free hole surfaces between the metal fibers have a round surface equivalent with a diameter of  $< 5 \mu\text{m}$ . The substrate can here be formed of a woven fabric, felt, or non-woven fabric.

Instead, the substrate can also be formed from a foil which has been produced from sintered metal powder.

In order to facilitate the deposition of the diffusion barrier layer, it is preferred to partially fill the interstices or open pores on the side of the substrate facing the diffusion barrier layer with metal particles, or a mixture of metal particles with ceramic particles, or a mixture of metal particles with glass particles, or a mixture of metal particles with ceramic and glass particles, which become sintered to the metal fibers or to the foil. The pore structure in the surface region is thereby finer and the surface smoother. In addition, the thus treated substrate can be subjected to a rolling process before or after sintering, in order to completely flatten the surface.

An open porosity formed by pores with a pore diameter of 20nm to 500nm is preferred, at least for the single layer of the diffusion barrier layer directly adjoining the membrane layer.

It is furthermore preferred that at least the single layer of the diffusion barrier layer directly adjoining the membrane layer has microcracks, wherein the width of the microcracks is  $< 5 \mu\text{m}$ .

At least for the single layer of the diffusion barrier layer directly adjoining the membrane layer, production by physical vapor phase deposition (PVD), par-

ticularly by cathode sputtering, is preferred. Furthermore, formation by chemical vapor phase deposition (CVD) or by a sol-gel process have also proved effective. Furthermore, at least the single layer of the diffusion barrier layer directly adjoining the membrane layer can be formed by particles with an average particle size  $< 0.5 \mu\text{m}$ , which are sintered together. Any method is suitable in order to form a nonmetallic, inorganic diffusion barrier layer which is rigid, non-self-supporting, open-pored and/or has microcracks, and which is brittle, compact, and well-bonded to the substrate.

The preferred thickness of the single layer of the diffusion barrier layer directly adjoining the membrane layer is in a range of about  $0.1 \mu\text{m}$  to  $5 \mu\text{m}$ .

Furthermore, the diffusion barrier layer can be covered on the surface facing away from the substrate with a seed layer, whose chemical composition at least partially corresponds to that of the membrane layer. Here, the seed layer need not necessarily be a closed layer, but instead can be composed of individual material islands which have no connections. By such a seed layer, the electrodeposition of the membrane layer can be accelerated, and at the same time made more uniform, and its adhesion to the diffusion barrier layer can be improved.

The at least one membrane layer is preferably formed of palladium or a palladium alloy. Particularly suitable here are also the palladium alloys Pd – 8 atomic % Cd, Pd – 8 atomic % Y, Pd – 5.7 atomic % Ce, or Pd – 25 atomic % Ag. Instead, any other hydrogen-permeable, closed metallic layer is suitable as the membrane layer.

A thickness in the range of about  $0.5 \mu\text{m}$  to  $15 \mu\text{m}$  is preferred for the at least one membrane layer.

The at least one membrane layer can be covered with catalytically active material on its surface facing away from the at least one diffusion barrier layer. Platinum, ruthenium and rhodium are particularly preferred here as catalytically active materials. Instead, the catalytically active alloys of platinum-palladium, ru-

thenium-palladium, rhodium-palladium, or palladium-rare earth metal have proved to be effective.

The problem is solved for the method in that at least the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed by means of PVD, CVD, a sol-gel process, or by sintering-on powder particles with a particle size  $< 0.5 \mu\text{m}$ , and that subsequently the at least one membrane layer is electrodeposited on the surface of the diffusion barrier layer facing away from the substrate.

The production of suitable single layers, adjoining the membrane layer and being open-pored and/or having microcracks, by cathode atomization or sputtering is known, for example, for TiN layers, from the publication "Influence of the sputtering gas on the preferred orientation of nanocrystalline titanium nitride thin films" (R. Banerjee, R. Chandra, P. Ayyub, *Thin Solid Films*, 405, (2002), 64-72).

The surface of the diffusion barrier layer facing away from the substrate is preferably covered with a seed layer whose chemical composition at least partially corresponds to that of the membrane layer. The deposition of the membrane layer can thereby be accelerated and made more uniform, and its adhesion to the diffusion barrier layer can be improved.

Figs. 1 and 2 are to explain in an exemplary fashion the structure of a composite membrane according to the invention and also a measuring device for the determination of the membrane properties.

Fig. 1 shows a composite membrane in cross section, and

Fig. 2 shows a measuring device for the determination of membrane properties.

Fig. 1 shows a composite membrane 1 which is composed of a flexible, metallic substrate 1a, a rigid, non-self-supporting, nonmetallic, inorganic diffusion barrier layer 1b, and a hydrogen-permeable, nonporous metallic membrane layer 1c of palladium. The diffusion barrier layer 1b can here be formed from several single layers, wherein at least the single layer of the diffusion barrier layer 1b di-

rectly adjoining the membrane layer 1c is open-pored and/or has microcracks, and at its surface facing away from the substrate 1a has an electrical resistivity of less than  $10 \Omega\text{cm}$  at a temperature of  $20^\circ\text{C}$ . The membrane layer 1c is electrodeposited on this conductive surface. If the diffusion barrier layer also has nonporous or crack-free single layers, these must be formed of a hydrogen-permeable material.

Fig. 2 shows a composite membrane 1 with the substrate 1a, the diffusion barrier layer 1b and the membrane layer 1c, wherein the composite membrane divides the interior of the measuring device 2 into two chambers 2a, 2b. The first chamber 2a of the measuring device 2, which is arranged on the side of the membrane layer 1c, has an inlet opening 2c for a gas 3 to be separated. The gas 3 flows to the composite membrane 1, where the gas fraction 4b (permeate) of the gas 3, for which the composite membrane 1 is permeable, passes through the composite membrane 1 into the second chamber 2b. The remaining gas 4a escapes through an outlet opening 2d, while the permeate 4b is drawn off through an opening 2e from the second chamber 2b.

The following examples 1-5 are to clarify in exemplary fashion the production of a composite membrane according to the invention. Finally, Table 1 shows the hydrogen permeation rates of these composite membranes, determined at different temperatures in a measuring device according to Fig. 2.

### Example 1

For the production of a composite membrane 1 an open-pored substrate 1a of stainless steel, 0.3 mm thick, was cleaned and coated on one side with a suspension which contained nickel powder having a particle size of  $< 1 \mu\text{m}$ , in order to fill large pores and to smooth out unevenness of the surface of the substrate 1a. The nickel powder was sintered with the substrate 1a for about 1 hour at  $600^\circ\text{C}$  to adhere firmly. The thus treated, cooled substrate 1a was then cleaned of still loose nickel particles in an ultrasonic bath. A diffusion barrier layer 1b made of TiN was

next applied to the treated surface of the substrate in a thickness of 2  $\mu\text{m}$  by cathode sputtering. The diffusion barrier layer 1b, consisting of only a single layer, was next directly electroplated with a 4  $\mu\text{m}$  thick membrane layer 1c of palladium on the electrically conductive surface facing away from the substrate 1a. The electrodeposition of the palladium took place from an alkaline electrolyte. The composite membrane 1 was then boiled in distilled water for about 10 min., in order to remove residues of electrolyte.

The separating behavior of this composite membrane 1 was determined by separate determination of the nitrogen and hydrogen throughflow rates in the measuring device 2 according to Fig. 2. For this purpose, the composite membrane 1 was exposed on the side of the membrane layer 1c, once to pure hydrogen and once to pure nitrogen (for pressure conditions, see description in Table 1), and the volume flow of permeate 4b through the composite membrane 1 was respectively measured. The ratio of the volume flows  $\text{H}_2/\text{N}_2$  is above all a measure of the impermeability of the membrane layer 1c or of the number of pores or defects in the membrane layer 1c. A value of  $\text{H}_2/\text{N}_2 < 500$  shows, for example, that the separating action of the composite membrane is small, and that the number or pores or defects in the membrane layer is high.

The  $\text{H}_2/\text{N}_2$  ratio for this composite membrane had a value of  $> 5,500$  at  $300^\circ\text{C}$  and a value of  $> 8,000$  at  $450^\circ\text{C}$ , which permits concluding that the separation behavior is optimum.

### Example 2

For the production of a composite membrane 1, as in Example 1, an open-pored substrate 1a of stainless steel, 0.3 mm thick, was cleaned and coated on one side with a suspension, which contained nickel powder with a particle size of  $< 1 \mu\text{m}$ , in order to fill large pores and to smooth out unevenness of the surface of the substrate 1a. The nickel powder was sintered with the substrate 1a for about 1

hour at 600°C to adhere firmly. The thus treated, cooled substrate 1a was then cleaned of still loose nickel particles in an ultrasonic bath. A diffusion barrier layer 1b made of TiN was next applied in a thickness of 2  $\mu\text{m}$  by cathode sputtering. The diffusion barrier layer 1b, consisting only of a single layer, was covered on the electrically conductive surface facing away from the substrate 1a by an impregnation process with palladium seeds which did not form a closed layer but were present in islands. The seeded surface of the diffusion barrier layer 1b was next directly electroplated with a membrane layer 1c of palladium, 4  $\mu\text{m}$  thick. The electrodeposition of the palladium took place from an alkaline electrolyte. The composite membrane was then boiled in distilled water for about 10 min., in order to remove residues of electrolyte.

### Example 3

For the production of a composite membrane 1 an open-pored substrate 1a of stainless steel, 0.25 mm thick, was cleaned. An aluminum oxide sol (e.g., Nya-col AL20<sup>®</sup> of the PQ Corporation) was applied to the substrate 1a on one side to form a diffusion barrier layer 1b consisting of two single layers, in order to fill large pores and to smooth out unevenness of the surface of the substrate 1a. The substrate 1a was dried and tempered for about 2 hours at 650°C, so that a scratch-proof aluminum oxide layer was formed as the first single layer of the diffusion barrier layer 1b. To finish the diffusion barrier layer 1b, a second single layer of TiN, 2  $\mu\text{m}$  thick, was then applied by cathode sputtering to the first single layer of aluminum oxide on the side facing away from the substrate 1a. The electrically conducting surface of the diffusion barrier layer 1b facing away from the substrate 1a or the second single layer was next directly electroplated with a membrane layer 1c of palladium, 5.5  $\mu\text{m}$  thick. The electrodeposition of the palladium took place from an alkaline electrolyte. The composite membrane 1 was then boiled in distilled water for about 10 min., in order to remove residues of electrolyte.

The separating behavior of this composite membrane was determined (see Example 1) by separate determination of the nitrogen and hydrogen throughflow rates. The  $H_2/N_2$  ratio had a value of 4,500 at 300°C and a value of > 7,000 at 400°C.

#### Example 4

For the production of a composite membrane 1 an open-pored substrate 1 of stainless steel, 0.25 mm thick, was cleaned in an ultrasonic bath, and was coated on one side by screen printing with a paste, which contained nickel powder having a particle size of  $\leq 1 \mu\text{m}$  and also an aluminum oxide sol (e.g., Nyacol AL20<sup>®</sup>). The paste was produced by mixing the nickel powder with a small amount of 2-propanol and was homogenized for about 3 min. in an ultrasonic bath. Thereafter, aluminum oxide sol was mixed in, and a screen printing paste was produced by stirring-in some  $HNO_3$ . Large pores of the substrate 1a were filled, and unevenness of the surface of the substrate 1a was smoothed out. After drying the paste, the nickel-aluminum oxide layer (which, because of the metallic fraction, is to be counted as substrate and not as diffusion barrier layer) and the substrate 1a were sintered at 600°C for about 2 hours, for firm adhesion. A diffusion barrier layer 1b of TiN, 1.5  $\mu\text{m}$  thick, was next applied by cathode sputtering to the thus-treated surface of the substrate 1a.

The diffusion barrier layer 1b was covered on the electrically conductive surface facing away from the substrate 1a by an impregnation process with palladium seeds, which did not form a closed layer but were present in islands. The seeded surface of the diffusion barrier layer 1b was then directly electroplated with a membrane layer 1c of palladium, 6.5  $\mu\text{m}$  thick. The electrodeposition of the palladium took place from an alkaline electrolyte. The composite membrane was then boiled in distilled water for about 10 min., in order to remove residues of electrolyte.

The separating behavior of this composite membrane was determined (see Example 1) by separate determination of the nitrogen and hydrogen throughflow rates. The  $H_2/N_2$  ratio had a value of 6,000 at 300°C and a value of > 8,000 at 400°C.

#### Example 5

For the production of a composite membrane 1 an open-pored substrate 1a of stainless steel, 0.3 mm thick, was cleaned. A diffusion barrier layer 1b of substoichiometric  $IrO_{0.7}$  was then applied to the cleaned surface of the substrate 1a in a thickness of 1.5  $\mu m$  by cathode sputtering. The diffusion barrier layer 1b, consisting of only a single layer, was next directly electroplated on the electrically conductive surface facing away from the substrate 1a with a 6  $\mu m$  thick membrane layer 1c of palladium-silver alloy containing 25 wt.% Ag. The composite membrane 1 was then boiled in distilled water for about 10 min., in order to remove residues of electrolyte.

The separating behavior of this composite membrane was determined (see Example 1) by separate determination of the nitrogen and hydrogen throughflow rates. The  $H_2/N_2$  ratio for this composite membrane had a value of 6,000 at 300°C and a value of > 8,000 at 400°C, which permits concluding that the separation behavior is optimum.

The following Table 1 shows the hydrogen permeation rates (under standard conditions) of the composite membranes from examples 1, 3, 4 and 5 after 50 hours of operation at different temperatures, wherein the gas pressure of the gas 3 to be separated had a value of 4 bar (absolute), and the gas pressure of the permeate 4b had a value of 1 bar (absolute). The surface area of the tested composite membrane was 10  $cm^2$  respectively.

Table 1

	H <sub>2</sub> Permeation Rate (m <sup>3</sup> /m <sup>2</sup> h)			
Temperature (°C)	Example 1	Example 3	Example 4	Example 5
300	51	32	24	72
400	85	54	42	81
450	98	-	-	-

Claims

1. Composite membrane, comprising a flexible, metallic substrate and a layer system arranged on at least one surface of the substrate, wherein the layer system is formed of a rigid, non-self-supporting, nonmetallic inorganic diffusion barrier layer and at least one hydrogen-permeable, nonporous, metallic membrane layer, wherein the diffusion barrier layer is arranged between the substrate and the at least one membrane layer and is formed of at least one single layer, wherein at least the single layer of the diffusion barrier layer directly adjoining on the membrane layer is open-pored and/or has microcracks and has an electrical resistivity of less than  $10 \Omega\text{cm}$  at a temperature of  $20^\circ\text{C}$  on its surface facing away from the substrate, and wherein the substrate has an open porosity in a range of 15% to 60%, and the at least one membrane layer is electrodeposited on the surface of the at least one diffusion barrier layer facing away from the substrate.
2. Composite membrane according to claim 1, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer has an electrical resistivity of less than  $10,000 \mu\Omega\text{cm}$  at a temperature of  $20^\circ\text{C}$  on its surface facing away from the substrate.
3. Composite membrane according to claim 1, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer has an electrical resistivity of less than  $1,000 \mu\Omega\text{cm}$  at a temperature of  $20^\circ\text{C}$  on its surface facing away from the substrate.
4. Composite membrane according to one of claims 1-3, characterized in that the substrate is formed of stainless steel.

5. Composite membrane according to one of claims 1-4, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of a metal nitride.
6. Composite membrane according to claim 5, characterized in that the metal nitride is formed with at least one metal of the group of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten.
7. Composite membrane according to claim 6, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of titanium nitride (TiN).
8. Composite membrane according to claim 6, characterized in that the metal nitride additionally contains aluminum besides the at least one metal of the group of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten.
9. Composite membrane according to one of claims 1-4, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of a metal oxide.
10. Composite membrane according to claim 9, characterized in that the metal oxide has a substoichiometry.
11. Composite membrane according to claim 10, characterized in that the metal oxide is a substoichiometric titanium oxide.

12. Composite membrane according to one of claims 9-10, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of ruthenium oxide ( $\text{RuO}$  or  $\text{RuO}_2$  or  $\text{Ru}_2\text{O}_3$ ).
13. Composite membrane according to one of claims 9-10, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of iridium oxide ( $\text{IrO}$  or  $\text{IrO}_2$  or  $\text{Ir}_2\text{O}_3$ ).
14. Composite membrane according to one of claims 9-10, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of rhodium oxide ( $\text{RhO}$  or  $\text{Rh}_2\text{O}_3$ ).
15. Composite membrane according to one of claims 1-4, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of a metal carbide.
16. Composite membrane according to claim 15, characterized in that the metal carbide is formed with at least one metal of the group of titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten.
17. Composite membrane according to claim 16, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of tungsten carbide  $\text{WC}$ .
18. Composite membrane according to one of claims 15-17, characterized in that the metal carbide contains included carbon.

19. Composite membrane according to one of claims 1-4, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of a metal oxynitride.
20. Composite membrane according to claim 19, characterized in that the metal oxynitride is formed with at least one metal of the group of titanium, zirconium and hafnium.
21. Composite membrane according to claim 20, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of titanium oxynitride.
22. Composite membrane according to claim 20, characterized in that the metal oxynitride additionally contains aluminum besides the at least one metal of the group of titanium, zirconium, and hafnium.
23. Composite membrane according to one of claims 1-4, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of a metal carbonitride.
24. Composite membrane according to claim 23, characterized in that the metal carbonitride is formed with at least one metal of the group of vanadium, niobium, tantalum, chromium, molybdenum and tungsten.
25. Composite membrane according to one of claims 24, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of titanium carbonitride (TiCN).

26. Composite membrane according to one of claims 24, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of  $\text{NbC}_x\text{N}_y$ .
27. Composite membrane according to claim 26, characterized in that the valence  $x$  assumes the value 0.3 and the valence  $y$  the value 0.7.
28. Composite membrane according to one of claims 1-4, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of a metal boride.
29. Composite membrane according to claim 28, characterized in that the metal boride is formed with at least one metal of the group of niobium, titanium, zirconium, cerium and barium.
30. Composite membrane according to claim 29, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed of  $\text{CeB}_6$  or  $\text{TiB}_2$  or  $\text{NbB}$  or  $\text{NbB}_2$ .
31. Composite membrane according to one of claims 1-30, characterized in that the substrate is formed of metal fibers, wherein the interstices between the metal fibers have a width and length respectively of  $< 5 \mu\text{m}$  or the free hole surfaces between the metal fibers have a round surface equivalent with a diameter of  $< 5 \mu\text{m}$ .
32. Composite membrane according to one of claims 1-31, characterized in that the substrate is formed as a foil from sintered metal powder.

33. Composite membrane according to one of claims 31-32, characterized in that the interstices or open pores on the side of the substrate facing the at least one diffusion barrier layer are at least partially filled with metal particles or a mixture of metal particles with ceramic particles and/or glass particles, which are sintered with the metal fibers or the foil.
34. Composite membrane according to one of claims 1-33, characterized in that at least the single layer of the diffusion barrier layer directly adjoining the membrane layer has an open porosity, wherein a pore diameter of the pores is 20nm to 500nm.
35. Composite membrane according to one of claims 1-34, characterized in that at least the single layer of the diffusion barrier layer directly adjoining the membrane layer has microcracks and that the width of the microcracks is  $< 5 \mu\text{m}$ .
36. Composite membrane according to one of claims 1-35, characterized in that at least the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed by PVD (physical vapor phase deposition).
37. Composite membrane according to claim 36, characterized in that at least the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed by cathode sputtering.
38. Composite membrane according to one of claims 1-37, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed by CVD (chemical vapor phase deposition).

39. Composite membrane according to one of claims 1-35, characterized in that at least the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed by a sol-gel process.
40. Composite membrane according to one of claims 1-35, characterized in that at least the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed by particles with a mean particle size  $< 0.5 \mu\text{m}$ , which are sintered together.
41. Composite membrane according to one of claims 1-40, characterized in that the single layer of the diffusion barrier layer directly adjoining the membrane layer has a thickness in a range of  $0.1 \mu\text{m}$  to  $5 \mu\text{m}$ .
42. Composite membrane according to one of claims 1-41, characterized in that the diffusion barrier layer is covered on the surface facing away from the substrate with a seed layer whose chemical composition at least partially corresponds to that of the membrane layer.
43. Composite membrane according to one of claims 1-42, characterized in that the at least one membrane layer is formed from palladium or a palladium alloy.
44. Composite membrane according to one of claims 1-43, characterized in that the at least one membrane layer has a thickness in a range of  $0.5 \mu\text{m}$  to  $15 \mu\text{m}$ .

45. Composite membrane according to one of claims 1-44, characterized in that the at least one membrane layer is covered on its surface facing away from the diffusion barrier layer with catalytically active material.
46. Composite membrane according to claim 45, characterized in that the catalytically active material is formed of platinum or ruthenium or rhodium.
47. Composite membrane according to claim 45, characterized in that the catalytically active material is formed of a platinum-palladium alloy or a ruthenium-palladium alloy or a rhodium-palladium alloy or a palladium-rare earth metal alloy.
48. Process for production of a composite membrane according to one of claims 1-47, characterized in that at least the single layer of the diffusion barrier layer directly adjoining the membrane layer is formed by means of PVD, CVD, a sol-gel process, or by sintering-on of powder particles with a mean particle size of  $< 0.5 \mu\text{m}$ , and that the at least one membrane layer is then electrodeposited on the surface of the diffusion barrier layer facing away from the substrate.
49. Process according to claim 48, characterized in that the surface of the diffusion barrier layer facing away from the substrate is covered with a seed layer whose chemical composition at least partially corresponds to that of the membrane layer.

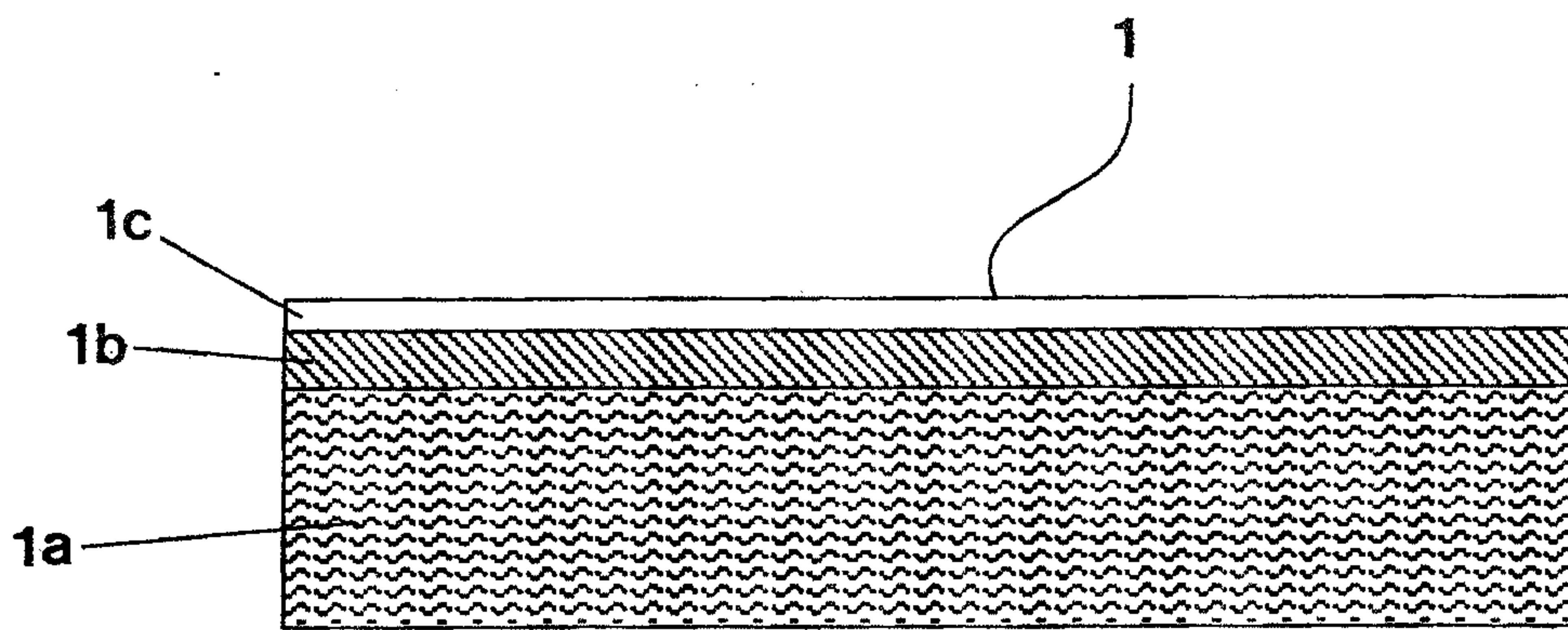


Fig.1

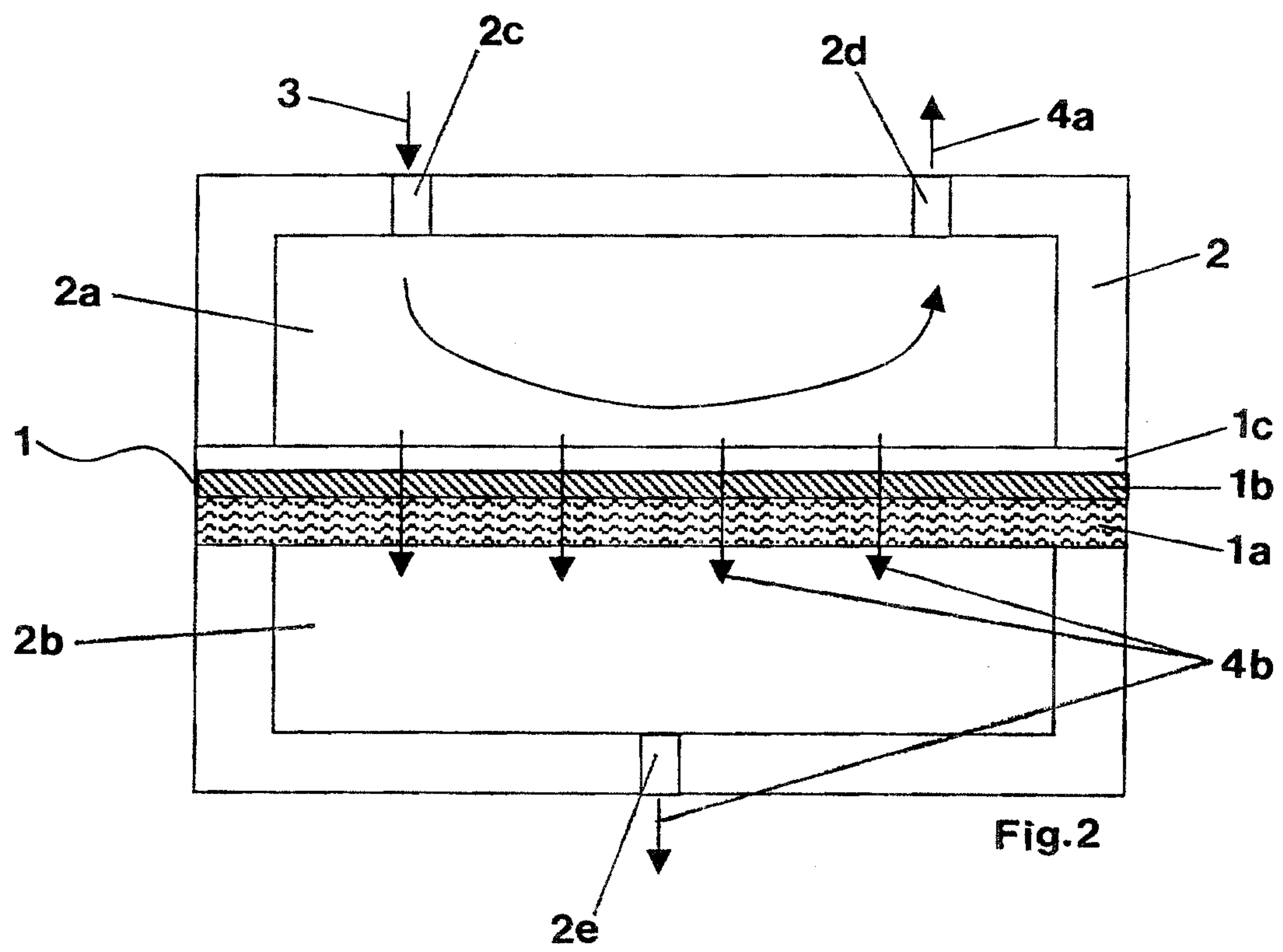


Fig.2

