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(72) Inventeur/Inventor:
DOHLE, HENDRIK, DE

(73) Propriétaire/Owner:
FORSCHUNGSZENTRUM JULICH GMBH, DE

(74) Agent: ROBIC

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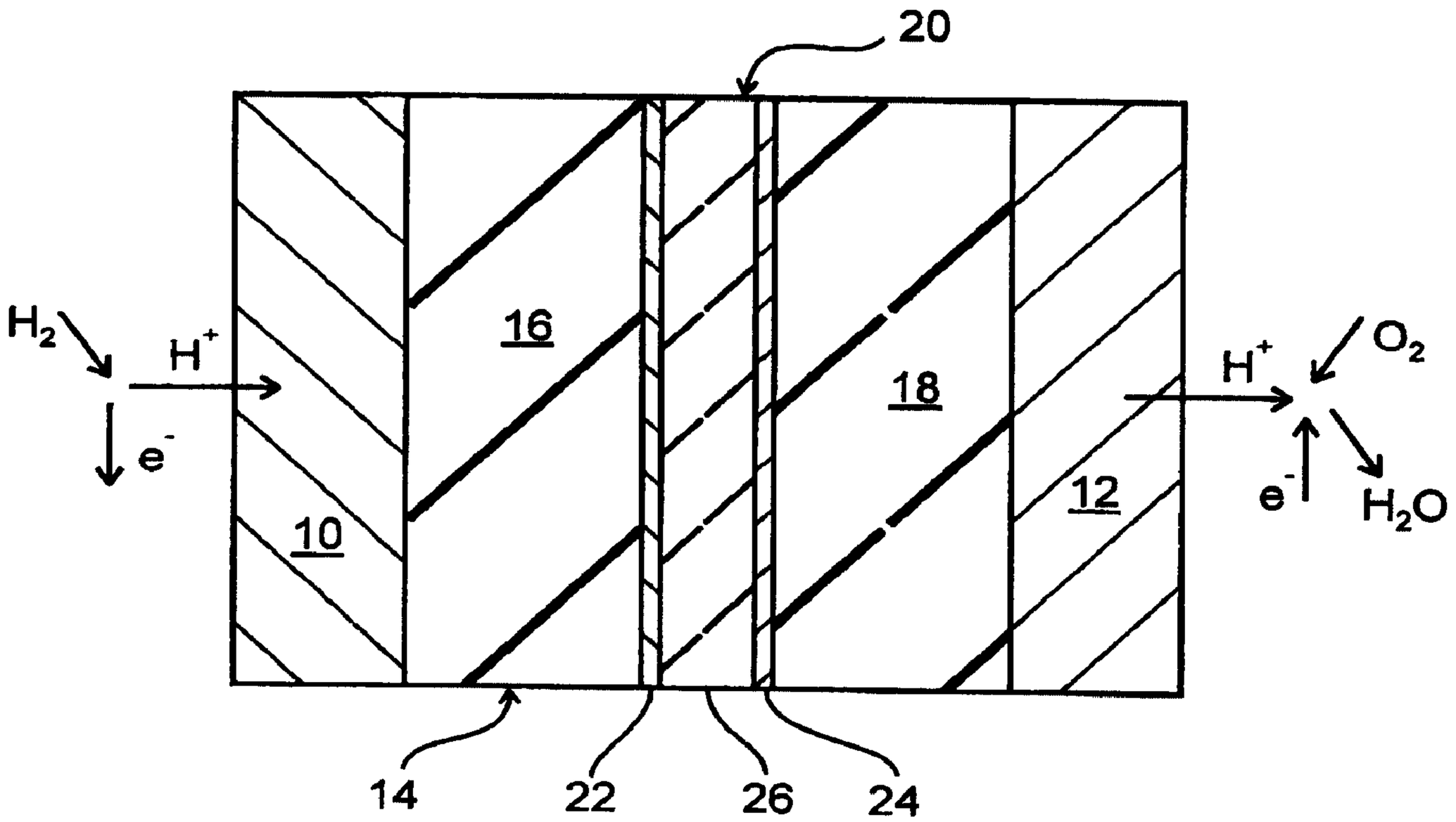
(54) Title: FUEL CELL WITH A PROTON CONDUCTING ELECTROLYTE



(57) Abrégé/Abstract:
Existing fuel cells with proton conducting electrolyte use a membrane made of perfluorinated plastic material as electrolyte and are powered using hydrogen or methanol as fuel. One disadvantage is that said electrolyte membrane allows both the protons and the fuel to pass through resulting in a loss in fuel cell efficiency. Migration of the fuel molecules through the electrolyte (14) from the anode side to the cathode side is prevented in such a way that the fuel cell exhibits a hydrogen permeable barrier layer composite (20) comprising two outer layers (22, 24) and a central layer (26) arranged between the latter. Each outer later is made of palladium and/or a palladium alloy and the central layer is made of niobium and/or tantalum and/or an alloy based on one of said metals. Palladium, niobium and tantalum exhibit high atomic hydrogen diffusibility but are impermeable to larger atoms and molecules. The barrier layer composite separates the anode gas space from the cathode gas space in such a way that the fuel cannot migrate through the electrolyte to the cathode side.

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(71) Anmelder *(für alle Bestimmungsstaaten ausser US)*: FORSCHUNGSZENTRUM JÜLICH GMBH [DE/DE]; Leo–Brandt–Strasse, D–52425 Jülich (DE).

(72) Erfinder; und
(75) Erfinder/Anmelder *(nur für US)*: DOHLE, Hendrik [DE/DE]; Cäcilienstrasse 53a, D–52249 Eschweiler (DE).

(74) Anwälte: HUBLE, Kai usw.; Bungartz, Hublé & Partner, Eupener Strasse 161a, D–50933 Köln (DE).

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(54) Title: FUEL CELL WITH A PROTON CONDUCTING ELECTROLYTE

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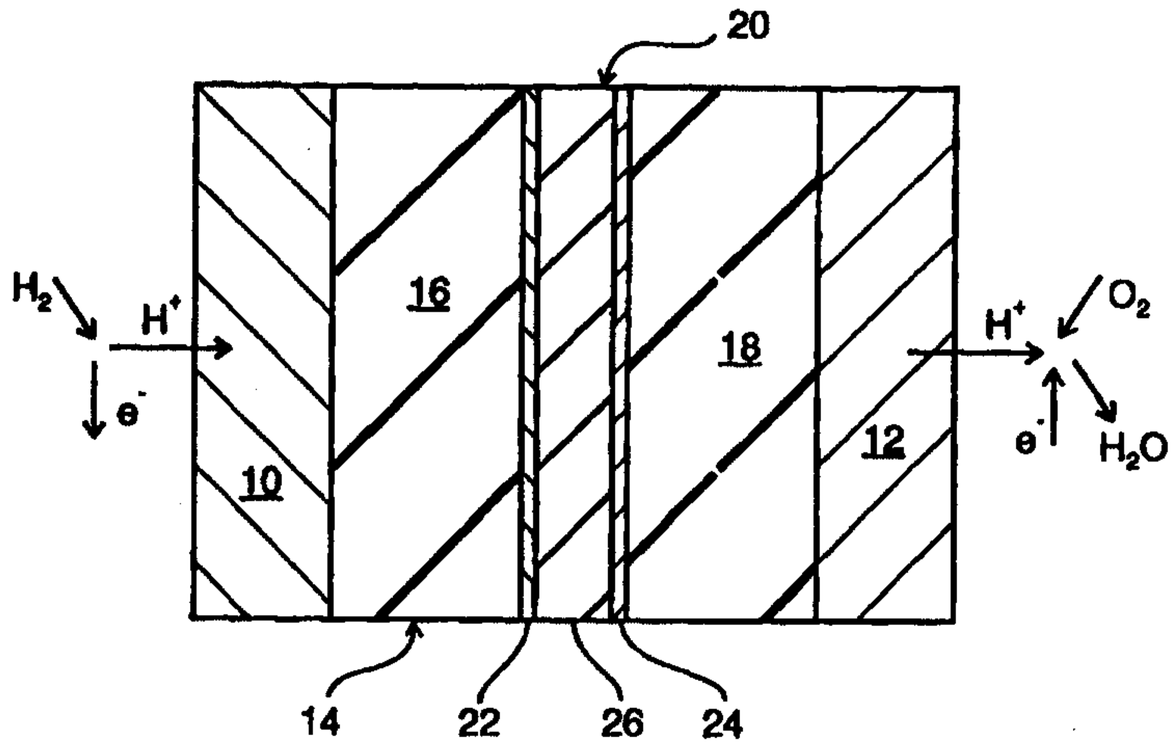
(57) Abstract

Existing fuel cells with proton conducting electrolyte use a membrane made of perfluorinated plastic material as electrolyte and are powered using hydrogen or methanol as fuel. One disadvantage is that said electrolyte membrane allows both the protons and the fuel to pass through resulting in a loss in fuel cell efficiency. Migration of the fuel molecules through the electrolyte (14) from the anode side to the cathode side is prevented in such a way that the fuel cell exhibits a hydrogen permeable barrier layer composite (20) comprising two outer layers (22, 24) and a central layer (26) arranged between the latter. Each outer later is made of palladium and/or a palladium alloy and the central layer is made of niobium and/or tantalum and/or an alloy based on one of said metals. Palladium, niobium and tantalum exhibit high atomic hydrogen diffusibility but are impermeable to larger atoms and molecules.
The barrier layer composite separates the anode gas space from the cathode gas space in such a way that the fuel cannot migrate through the electrolyte to the cathode side.



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FUEL CELL WITH A PROTON CONDUCTING ELECTROLYTE

The invention relates to a fuel cell with a proton conducting electrolyte, an anode, and a cathode.

In fuel cells, the chemical energy stored in the fuel is directly converted into electrical energy and heat. As fuel there are used for example pure hydrogen, methanol, or natural gas, and the fuel reacts in the in fuel cell with the oxidant, which in most cases is pure oxygen or the oxygen contained in the air. In this reaction, aside from electrical energy and heat there is also produced water, and when using carbonic fuels, in addition carbon dioxide. Fuel and oxidant together are referred to as operating material.

The single fuel cell comprises an anode and a cathode, between which the electrolyte is disposed. The fuel is continuously fed to the fuel cell's anode gas space laying before the anode, the oxidant is continuously fed to the fuel cell's cathode gas space laying before the cathode, the reaction products are continuously carried away. The different types of fuel cells are commonly classified using the employed electrolyte. Electrolytes being conductive for protons are used in fuel cells, in which protons are separated at the anode from the fuel while releasing electrons. The protons migrate through the proton conducting electrolyte to the cathode, where they react with the oxygen to form water while incorporating electrons.

One example for such fuel cells is the so-called polymer membrane fuel cell which employs as electrolyte a membrane made of perfluorinated plastic material. At present, semipermeable membranes on the basis of poly(perfluoroalkene) sulfonic acid, as for example Nafion® R 117 of Du Pont are mainly used. For the production of the fuel cell, one face of the electrolyte membrane is coated with the anode material which usually is platinum or a platinum-ruthenium alloy, and the opposite face is coated with the cathode material which preferably is platinum.

The polymer membrane fuel cell can be operated with hydrogen or methanol. When using methanol, it is also referred to as direct methanol fuel cell. The electrode reactions of the polymer membrane fuel cell operated with hydrogen read as follows:

anode: $H_2 \rightarrow 2\,H^+ + 2\,e^-$

cathode: $O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$

The electrode reactions of the direct methanol fuel cell read as follows:

anode: $CH_3OH + H_2O \rightarrow CO_2 + 6\,H^+ + 6\,e^-$

cathode: $O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$

One disadvantage of these known polymer membrane fuel cells is that the electrolyte membrane allows both the protons and, though in a smaller extent, the fuel, that is the molecular hydrogen (H_2) or the methanol molecules (CH_3OH), to pass through. This results in a loss in fuel cell efficiency. In case of the direct methanol fuel cell this unwelcome effect is made worse because the water (H_2O) existing on the anode side as well as on the cathode side, as well penetrates into the Nafion foil so that said foil swells up and allows even more methanol to pass through.

It is the object of the invention to prevent in a fuel cell of the type mentioned at the beginning, the migration of the fuel through the proton conducting electrolyte from the anode side to the cathode side.

This object is achieved in such a way that the fuel cell comprises at least one hydrogen permeable barrier layer composite comprising two outer layers and a core layer arranged there between, each outer layer being essentially made of palladium and/or an alloy on the basis of palladium, and the core layer being essentially made of niobium and/or tantalum and/or an alloy on the basis of one of these metals.

Preferably, the layer composite according to the invention is essentially made of the metals palladium, niobium, and tantalum, which exhibit a high diffusibility to atomic hydrogen but on the other hand are impermeable to larger atoms and molecules, in

particular molecular hydrogen, water and methanol. The barrier layer composite serves to separate the anode gas space from the cathode gas space in such a way that the fuel cannot migrate through the electrolyte from the anode side to the cathode side. The incorporation of the hydrogen in the metal lattice occurs while forming metal hydride.

Preferably, the three-layer design is based on the following considerations: tantalum exhibits a high diffusibility to hydrogen atoms which is higher than that of palladium. On the other hand, the energy required for the transition of the hydrogen from the gas phase into the hydride phase is lower in the case of palladium than in the case of tantalum. However, palladium is more expensive than tantalum. These correlations are as well valid for niobium which is chemically allied with tantalum. The barrier layer composite according to the invention is cheaper than a diffusion layer essentially made of palladium, because the outer layers can be made very thin, and it incorporates the hydrogen easier than a diffusion layer essentially made of tantalum and/or niobium. The two outer layers essentially made of palladium provide, because of the low transition energy, for an easy incorporation of the hydrogen from the gas phase into the outer layer, and the subsequent transition from the outer layer into the core layer requires only a much lower energy than the transition from the gas phase into tantalum or niobium. Since the material of the core layer is relatively cheap, the latter can be made almost as thick as desired and thus provide for the stability of the barrier layer composite.

There are several possibilities for the arrangement of each barrier layer composite relative to the electrolyte.

A first variant is that the electrolyte comprises two plies between which is arranged a barrier layer composite. This arrangement has the advantage that the electrolyte which contains in its interior the barrier layer composite, can be coated with the electrode materials exactly like a usual electrolyte without barrier layer composite.

According to a second variant, a barrier layer composite is arranged between one of the electrodes and the electrolyte.

According to a third variant, at least one of the electrodes is formed as a barrier layer composite. For example, the anode may be substituted by a barrier layer composite according to the invention which performs the anode's function so that, in contrast to the first and second variant, it is possible to dispense with a separate anode layer, that is an anode layer provided in addition to the barrier layer composite.

The barrier layer composite may comprise aside from the mentioned three layers further layers as well which are arranged on the anode side and/or the cathode side between the respective outer layer and the core layer. The material of these additional intermediate layers may be chosen for example in view of facilitating the transition of the hydrogen from the anode sided outer layer into the core layer or from the core layer into the cathode sided outer layer.

In a first alternative, the intermediate layer is essentially made of an alloy which essentially contains the main component of the adjoining outer layer and the main component of the core layer. Therefore, if the two outer layers are made of a palladium alloy and the core layer is made of a niobium alloy then, for example, an intermediate layer which is essentially made of a palladium-niobium alloy may be arranged between each outer layer and the core layer.

In a second alternative, the intermediate layer is essentially made of a mixture which essentially contains the material of the adjoining outer layer and the material of the core layer. Therefore, the intermediate layer may not only be available as an alloy but as well in a different form which depends on the employed manufacturing process. The intermediate layer may be deposited on the core layer for example by sputtering, the sputtering being carried out by using in a first step the material of the core layer and in a second step the material of the outer layer.

A third alternative refers to the case where the core layer is essentially made of tantalum and/or an alloy on the basis of tantalum, and according to this alternative, the

intermediate layer is essentially made of niobium and/or vanadium and/or an alloy on the basis of one of these metals and/or an palladium-tantalum alloy. Therefore, the intermediate layer may contain metals which are not contained in the core layer and the outer layer.

It is preferred that the outer layers are essentially made of a palladium-silver alloy, preferably with a content of silver of at least 25% by weight. For a palladium foil blows up considerably when incorporating hydrogen, and becomes brittle and cracky. The dimensional stability is improved by the addition of silver.

The core layer preferably is a foil. The other layers may be deposited on the core layer one after the other by coating. The coating may be carried out by sputtering, powder coating, vacuum evaporation, and the like. The other layers may as well be foils. In this case, the deposition of these foil layers may be carried out by laminating.

Since the core layer is made of a material which in comparison with the outer layers does have a higher transition energy but also a better diffusibility to hydrogen to make up, it may be thicker than each of the other layers and thus provide for the desired stability of the barrier layer composite, of the electrolyte membrane, or even of the whole fuel cell.

In the following, preferred embodiments of the invention will be described more precisely by way of example with reference to the enclosed drawing.

FIG. 1 is a schematic cross-sectional view of a polymer membrane fuel cell in a first embodiment;

FIG. 2 is a schematic cross-sectional view of a polymer membrane fuel cell in a second embodiment;

FIG. 3 is a schematic cross-sectional view of a polymer membrane fuel cell in a third embodiment; and

FIG. 4 and 5 show in an enlarged detail view modifications of the barrier layer composite of the fuel cells shown in the FIG. 1 to 3.

The FIG. 1 shows schematically the design of a polymer membrane fuel cell in a first embodiment. The fuel cell comprises an anode 10 and a cathode 12 as well as an electrolyte 14 placed there between. On the left side of the anode 10 there is the so-called anode gas space, and on the right side of the cathode 12 there is the cathode gas space. The electrolyte 14 is a proton conducting membrane in the form of a foil made of Nafion® R 117 which is coated on its left side in the FIG. 1 with the anode 10 and on its right side with the cathode 12. For the electrodes 10, 12 there are used catalytic materials which are chosen in view of the reactions occurring at the electrodes 10, 12, such as for example the separation of protons at the anode 10 and the recombination and reaction of the protons to form water at the cathode 12. Possible materials are above all noble metals, and preferably platinum and gold are used, and for the anode 10 platinum-ruthenium alloys as well. The electrode material is usually deposited wet-chemically on the electrolyte membrane 14, or is hot pressed as a powder therewith. The electrolyte 14 is approximately 200 µm thick, each of the electrodes 10, 12 is approximately 100 µm thick.

According to the first embodiment of the fuel cell as shown in the FIG. 1, the electrolyte 14 is divided in two plies 16, 18 of equal size between which a barrier layer composite 20 is positioned. Therefore, the barrier layer composite 20 separates the anode gas space from the cathode gas space. The composite 20 consists of two outer layers 22, 24 and a core layer 26 positioned there between. Each outer layer 22, 24 is made of palladium and is approximately 0,5 µm thick whereas the core layer 26 is an approximately 50 to 100 µm thick foil made of tantalum. For the production of the composite 20, the outer layers 22, 24 have been deposited on the core layer foil 26 by sputtering.

The thickness of the barrier layer composite 20 is chosen in view of the barrier function, but for cost reasons – palladium is more expensive than tantalum – the core layer 26 in comparison with the outer layers 22, 24 should be as thick as possible. The outer layers 22, 24 must be at least so thick that the hydrogen atoms can enter

the core layer 26 as easily as possible and exit it again on the other side as easily as possible.

With reference to the embodiment of a fuel cell as shown in the FIG. 1, the manner of function of a polymer membrane fuel cell operated with hydrogen will now be described.

Molecular hydrogen H_2 is continuously fed as fuel to the anode gas space. At the anode 10, a hydrogen molecule H_2 is catalytically separated in two protons H^+ and two electrons e^-. The electrons e^- are led through a current collector (not shown) to an electrical consumer (not shown too). They reach the cathode 12 from the consumer via a second current collector (not shown).

The protons H^+ produced at the anode 10 enter the anode sided electrolyte ply 16 and migrate through the latter up to the anode sided outer layer 22. There they recombine with electrons e^- to form hydrogen atoms H which are incorporated in the outer layer 22 while forming palladium hydride. The electrons e^- required for the recombination come from the cathode sided outer layer 24, as will be explained in the following, and have migrated through the core layer 26.

The hydrogen atoms H dissolved in the palladium of the outer layer 22 diffuse through the metal lattice up to the interface with the core layer 26 where they enter the latter while forming tantalum hydride. They diffuse through the core layer 26, further into the cathode sided outer layer 24 while converting into tantalum hydride, and exit the latter into the cathode sided electrolyte ply 18 while separating into protons H^+ and electrons e^-. These electrons e^- migrate, as mentioned above, through the cathode sided outer layer 24 and the core layer 26 to the anode sided outer layer 22. Through the cathode sided electrolyte ply 18, the protons H^+ reach the cathode 12 where they combine with the electrons e^- fed via the external consumer circuit, and with the oxygen O_2 continuously fed to the cathode gas space, to form water H_2O. The reaction product water H_2O is continuously carried away from the cathode gas space.

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Therefore, the barrier layer composite 20 allows only atomic hydrogen H to pass through whereas it serves as a barrier for the molecular hydrogen H_2.

Aside from the arrangement of the barrier layer composite 20 in the interior of the electrolyte 14 as shown in the FIG. 1, other arrangements are possible as well, according to which the barrier layer composite 20 is arranged at the anode sided or at the cathode sided surface of the electrolyte 14, as will be described more precisely in the following with reference to the FIG. 2 and 3.

In the FIG. 2, there is shown a polymer membrane fuel cell in a corresponding second embodiment, according to which the barrier layer composite 20 is placed at the anode side of an one-ply electrolyte 14. This arrangement is in particular appropriate for the direct methanol fuel cell because it avoids that the water H_2O which is fed to the anode gas space penetrates into the electrolyte 14 and the latter swells up. As can be seen, the anode sided outer layer 22 borders on the anode 10 first, and the electrolyte 14 borders only on the cathode sided outer layer 24.

With reference of the embodiment of a fuel cell as shown in the FIG. 2, the manner of function of a direct methanol fuel cell will now be described.

Methanol CH_3OH and water H_2O are continuously fed to the anode gas space, and at the anode, they react to form carbon dioxide CO_2, protons H^+, and electrons e^-. The electrons e^- are led through a consumer circuit (not shown) to the cathode 12, as was already explained in connection with the FIG. 1. The protons H^+ recombine with electrons e^- coming from the cathode sided outer layer 24 and enter the anode sided outer layer 22 while forming metal hydride, they diffuse through the barrier layer composite 20 as described before, and, from the cathode sided outer layer 24, they reach as protons H^+ the electrolyte 14 while separating electrons e^-. The protons H^+ migrate through the electrolyte 14 to the cathode 12 where they react with the electrons e^- from the consumer circuit and with the oxygen O_2 continuously fed to the cathode gas space, to form water H_2O which is continuously carried away.

Therefore, the barrier layer composite 20 allows only atomic hydrogen H to pass through whereas it serves as a barrier between the two gas spaces for larger molecules, that is in particular methanol CH_3OH and water H_2O.

The fuel cell shown in the FIG. 2 may be manufactured in the following way. First, the two outer layers 22, 24 are deposited on the core layer 26, for example by sputtering. Then, the anode 10 is deposited on the anode sided outer layer 22, which may be carried out by sputtering as well. On the cathode sided outer layer 24, the electrolyte 14 is deposited. The face of the electrolyte 14 opposite to the outer layer 24 is coated with the cathode 12, for example by sputtering or chemical wet-deposition.

The FIG. 3 shows a polymer membrane fuel cell in a third embodiment which represents a modification of the fuel cell shown in the FIG. 2. According to this modification, the anode layer 10 of the fuel cell of the FIG. 2 is missing and instead the anode sided outer layer 22 of the FIG. 2 serves as anode; so to speak, the outer layer 22 of the FIG. 2 and the anode 10 of the FIG. 2 are combined in a combination layer 28. This combination layer 28 is essentially made of a mixture which contains as a first component the material of the anode 10 of the FIG. 2, that is for example platinum, and as second component the material of the outer layer 22 of the FIG. 2, that is for example palladium. This mixture may be an alloy of these metals but other types of mixture are possible as well. The combination layer 28 may be deposited on the core layer 26 by sputtering using a platinum-palladium alloy as target material.

However, the unchanged outer layer 22, that is the outer layer 22 without addition of platinum, may also be used as anode because the anode reactions even occur with palladium as catalyst.

The modification described above in connection with the FIG. 3 may be transferred analogously to the cathode side. In this case the cathode sided outer layer 24 of the FIG. 2 serves, on its own or as combination layer, as cathode.

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It is emphasized that the two outer layers 22, 24 may as well be made of different materials. For example, the content of palladium may be different, or the one outer layer may be made of palladium and the other may be made of a palladium-silver alloy. The core layer 26 too must not necessarily contain tantalum as main component. Possible main components are as well niobium or a mixture of tantalum and niobium, as well as niobium alloys, tantalum alloys, and niobium-tantalum alloys. The core layer 26 may as well comprise additions of substances contained in the outer layers 22, 24. In addition, at least one further intermediate layer may be positioned between each outer layer 22, 24 and the core layer 26.

In the FIG. 4 there is shown a modification of the barrier layer composite 20 used in the fuel cells shown in the FIG. 1, 2 and 3. Between the core layer 26 and the anode sided outer layer 22, there is arranged an intermediate layer 30. The intermediate layer 30 may be essentially made of an alloy which contains essentially the main component of the adjoining, anode sided outer layer 22 and the main component of the core layer 26, but it may as well be essentially made of a mixture which contains essentially the material of the adjoining, anode sided outer layer 22 and the material of the core layer 26. Therefore, if for example the core layer 26 is made of a tantalum alloy and the anode sided outer layer 22 is made of a palladium-silver alloy then the material for the intermediate layer 30 may be a palladium-tantalum alloy, but for example as well a mixture, preferably an alloy, of the palladium-silver alloy and the tantalum alloy.

However, other materials for the intermediate layer 30 are possible as well, as far as they offer a sufficient diffusibility to the hydrogen atoms. For example, in case of the core layer 26 and the outer layer 22 of the previous example, the intermediate layer 30 may as well be essentially made of niobium or a niobium alloy or vanadium or a vanadium alloy or a mixture, preferably an alloy, of two or more of these substances. In a similar manner, intermediate layers 32 may be arranged between the cathode sided outer layer 24 and the core layer 26 as well, as is shown in the FIG. 5.

WHAT IS CLAIMED IS:

1. Fuel cell with a proton conducting electrolyte (14), an anode (10) and a cathode (12), characterized in that it comprises at least one hydrogen permeable barrier layer composite (20) comprising two outer layers (22, 24) and a core layer (26) arranged there between, in that each outer layer (22, 24) is made of palladium and/or an alloy on the basis of palladium, and in that the core layer (26) is made of niobium and/or tantalum and/or an alloy on the basis of one of these metals.

2. Fuel cell according to claim 1, characterized in that the electrolyte (14) comprises two plies (16, 18) between which is arranged the barrier layer composite (20).

3. Fuel cell according to claim 1 or 2, characterized in that the barrier layer composite (20) is arranged between one of the electrodes (10, 12) and the electrolyte (14).

4. Fuel cell according to anyone of claims 1 to 3, characterized in that at least one of the electrodes (10, 12) is formed as a barrier layer composite (20).

5. Fuel cell according to anyone of claims 1 to 4, characterized in that at least one intermediate layer (30, 32) is arranged at least between one of the outer layers (22, 24) and the core layer (26).

6. Fuel cell according to claim 5, characterized in that the intermediate layer (30, 32) is essentially made of an alloy which contains the main component of the adjoining outer layer (22, 24) and the main component of the core layer (26).

7. Fuel cell according to claim 5, characterized in that the intermediate layer (30, 32) is made of a mixture which contains a material of the adjoining outer layer (22, 24) and a material of the core layer (26).

8. Fuel cell according to claim 5, characterized in that the core layer (26) is made of tantalum and/or an alloy on the basis of tantalum, and in that the intermediate layer (30, 32) is made of niobium and/or vanadium and/or an alloy on the basis of one of these metals and/or a palladium-tantalum alloy.

9. Fuel cell according to anyone of claims 1 to 8, characterized in that at least one of the outer layers (22, 24) is made of a palladium-silver alloy.

10. Fuel cell according to claim 9, characterized in that the content of silver is at least 25% by weight.

11. Fuel cell according to anyone of claims 1 to 10, characterized in that the core layer (26) is a foil.

12. Fuel cell according to anyone of claims 1 to 11, characterized in that at least one of the outer layers (22, 24) is a foil.

13. Fuel cell according to anyone of claims 1, 2, 3, 4, 5, 6, 7, 9, 10, 11 and 12, characterized in that the core layer (26) is thicker than each of the outer layers.

14. Fuel cell according to claim 8, characterized in that the core layer (26) is thicker than each of the outer and intermediate layers.

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FIG. 1

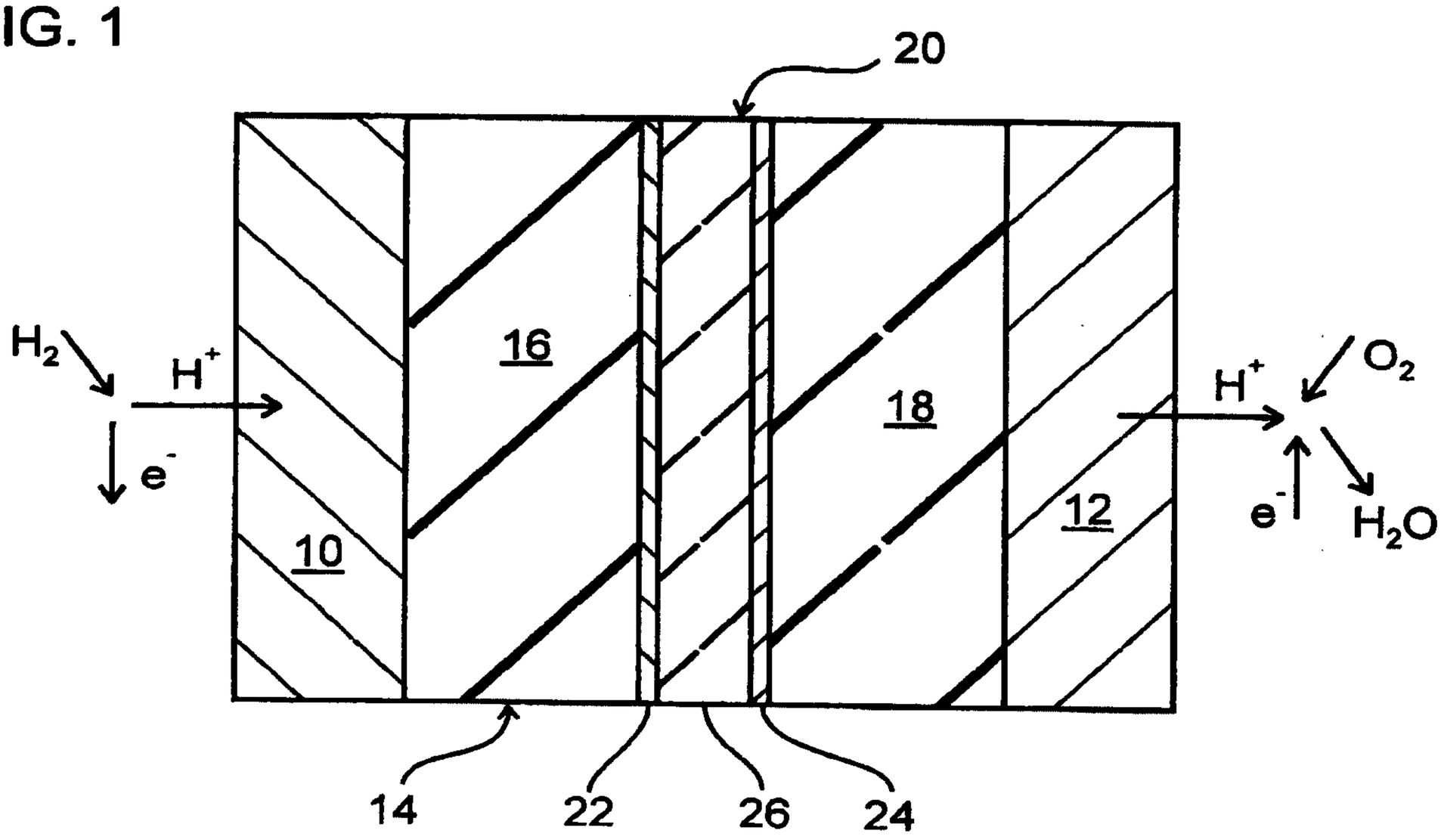

FIG. 2

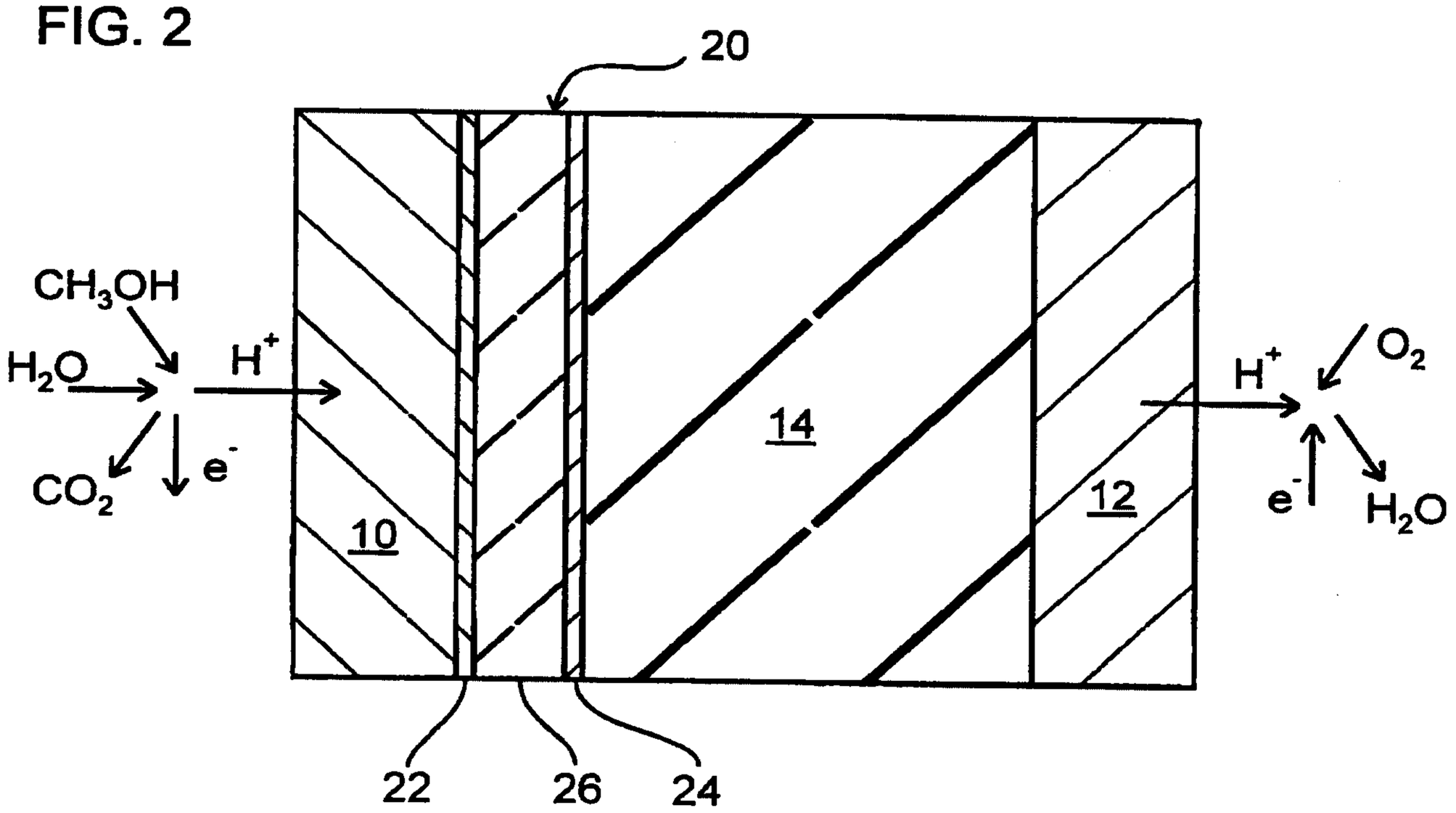

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FIG. 3

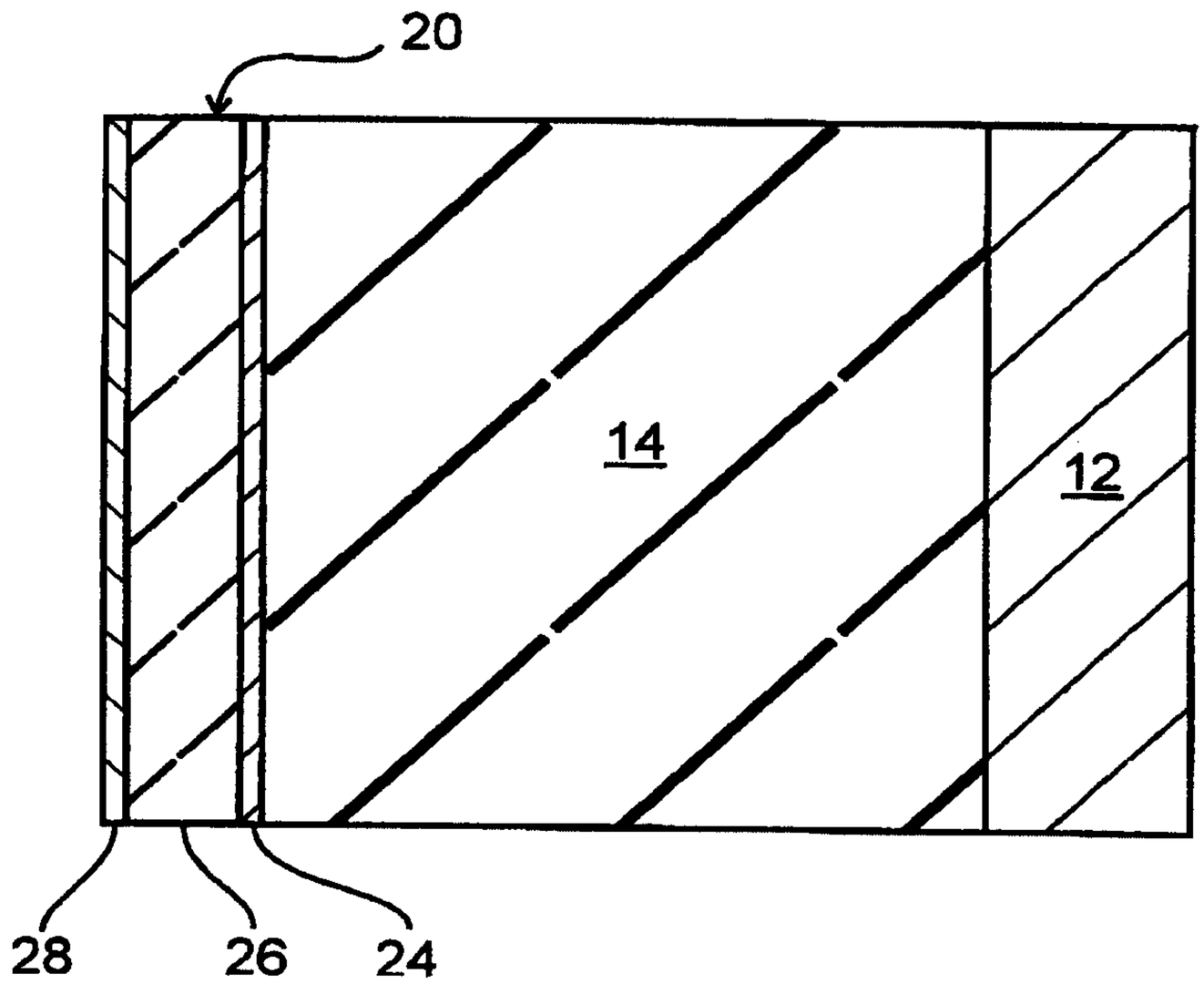


FIG. 4

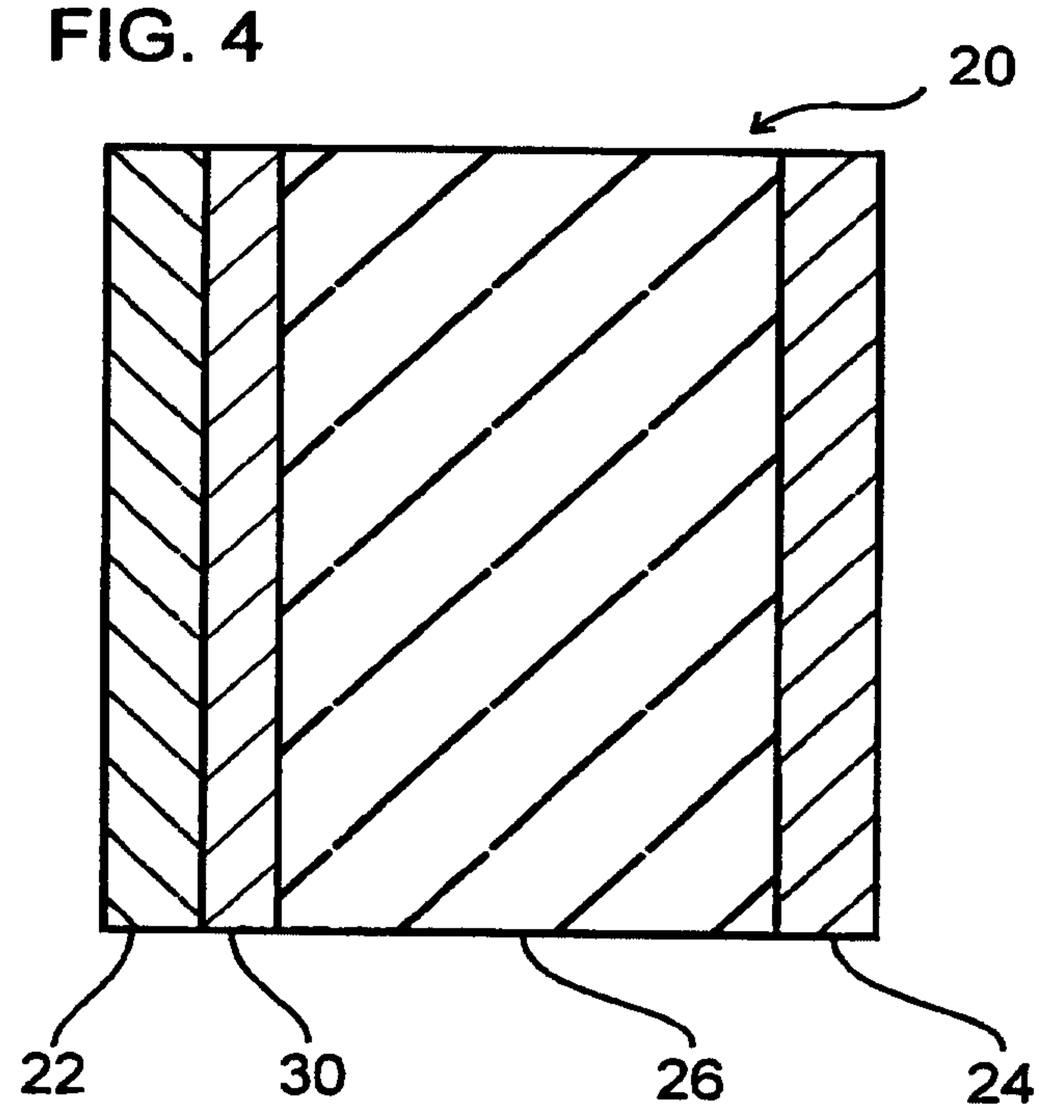
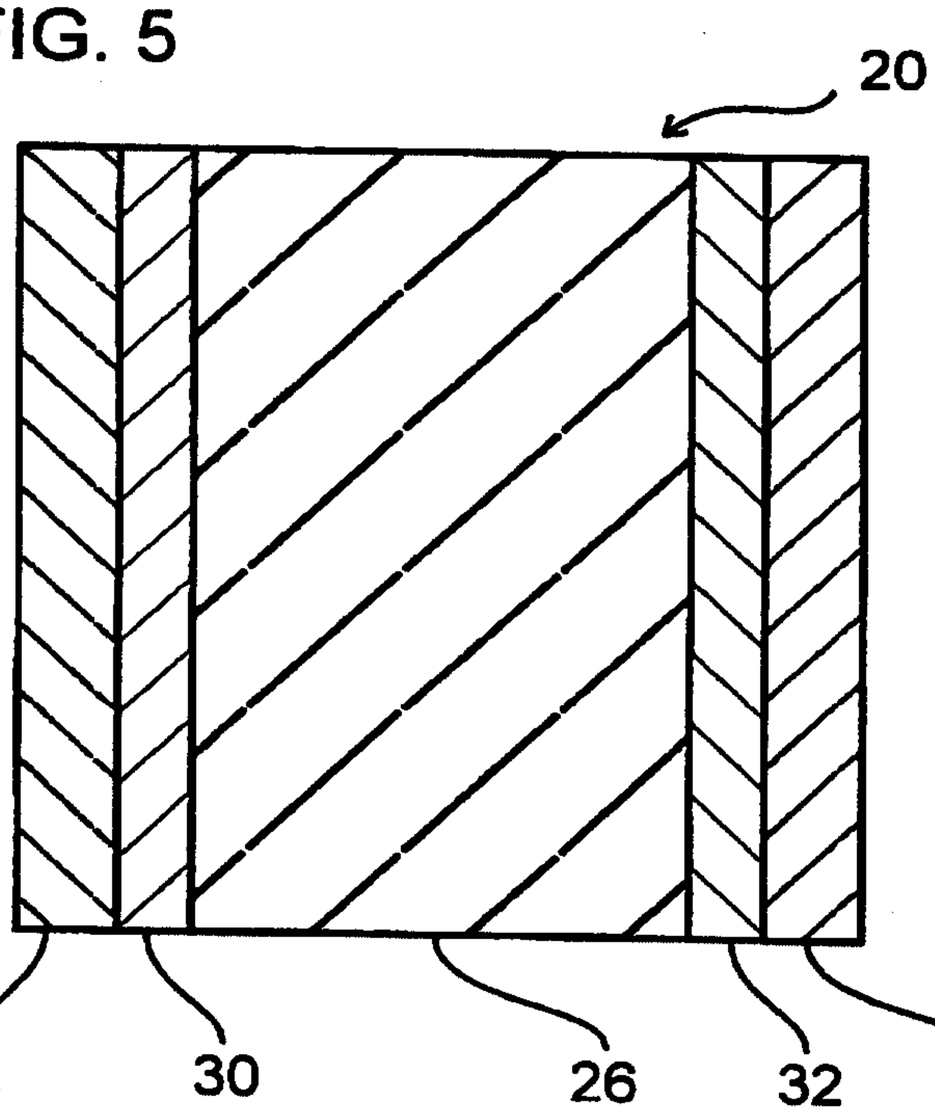
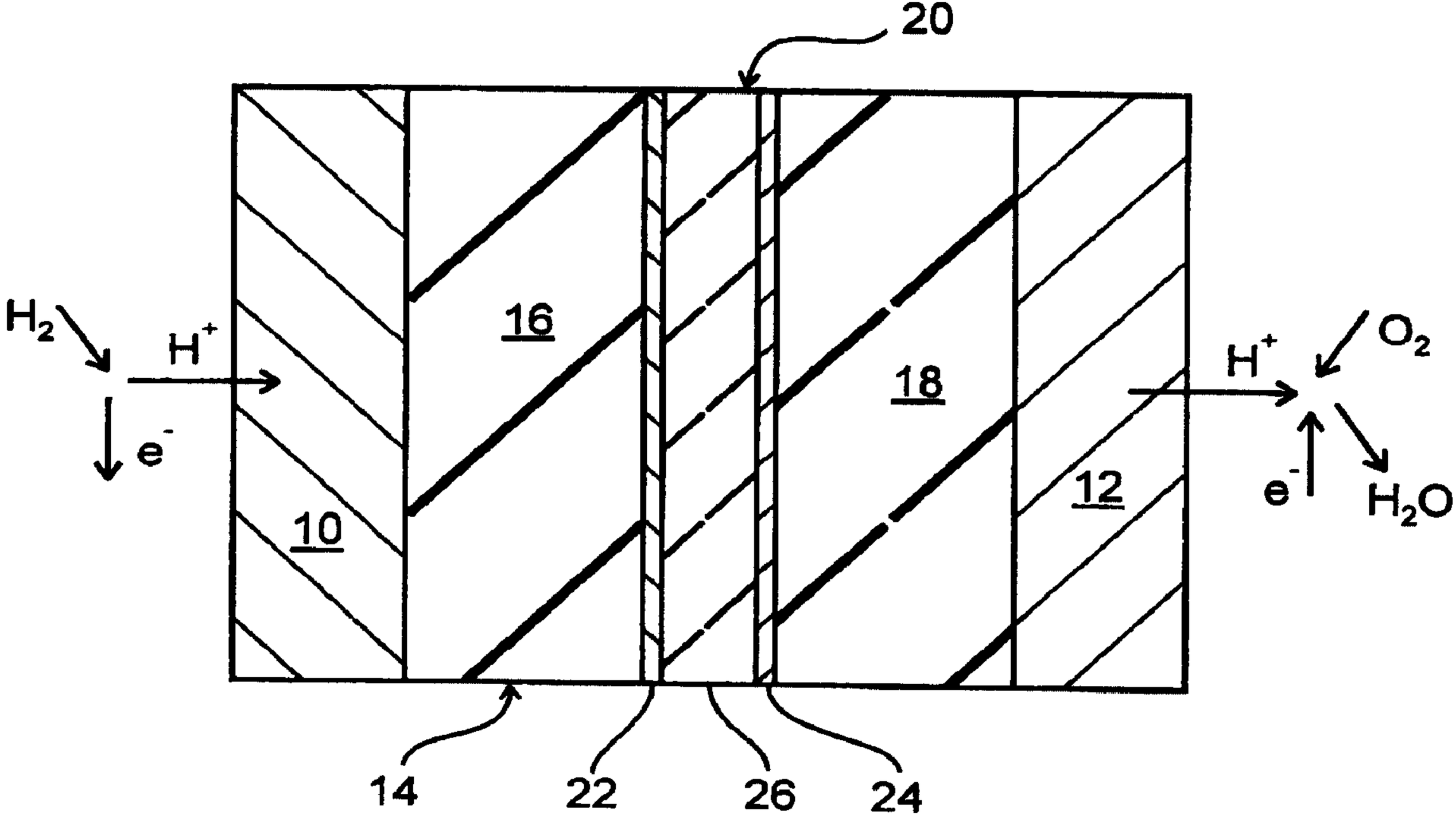


FIG. 5

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