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**A porous, gas permeable layer substructure for a thin, gas tight layer for use as a functional component in high temperature fuel cells**

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**WATERMARK PATENT and TRADEMARK ATTORNEYS,Locked Bag 5,HAWTHORN VIC 3122**

Abstract

The porous, gas permeable layer substructure (5; 5a, 5b) for a thin, gas impervious layer (89) can in particular be used as a functional component in high temperature fuel cells (8). This layer substructure has a smooth surface (50a) which is suitable for an application of the gas impervious layer or a multi-layer system including the gas impervious layer, with the application being carried out by means of a screen printing method or other coating methods. The smooth surface is formed by a compacted edge zone (50). The edge zone and a carrier structure (51) adjacent to this are made from a uniform substance mixture of sinterable particles. The porosity of the carrier structure is greater than 30 volume percent, preferably greater than 40 volume percent. The pore size of the edge zone is smaller than 10 μm, preferably smaller than 3 μm.

(Fig. 5)

Claims

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A porous, gas permeable layer substructure (5; 5a, 5b) for a thin, gas impervious layer (89), in particular for use as a functional component in high temperature fuel cells (8), which layer substructure has a smooth surface (50a) which is suitable for an application of the gas impervious layer or a multi-layer system including the gas impervious layer by means of a screen printing method or other coating methods, characterised in that the smooth surface is formed by a compacted edge zone (50); in that the edge zone and a carrier structure (51) adjacent to this are made from a uniform substance mixture consisting of sinterable particles; in that the porosity of the carrier structure is greater than 30 volume percent, preferably greater than 40 volume percent; and in that the pore size of the edge zone is smaller than 10 μm, preferably smaller than 3 μm.

2. A substructure for a layer in accordance with claim 1, characterised in that the porosity of the edge zone (50) is smaller than 30 volume percent, preferably smaller than 10 volume percent; and in that the thickness of the edge zone is smaller than 100 μm, preferably smaller than 30 μm.

3. A substructure for a layer in accordance with claim 1 or claim 2, characterised in that it is made up of a first layer (5') including the edge zone (50) and at least one second porous layer (5"), with the layers being sintered to form a cohesive structure and the second layer having a greater porosity than the first.

4. A substructure for a layer in accordance with any of claims 1 to 3, characterised in that it is formed in plate shape (5) or in that it has a tubular shape (81, 82), with the edge zone preferably forming the outer surface of the tube (81, 82).

5. An electrochemically active element (81, 82; 91, 92), in particular a high temperature fuel cell (8) or an oxygen generator (9) having a substructure (5a, 5b) in accordance with any of claims 1 to 4 and a multi-layer system which comprises an anode layer (55a, 50b), a gas impervious solid electrolyte layer (89) and a cathode layer (50a, 55b), with each of the electrode layers, that is either the anode layer (50b) or the cathode layer (50a), being formed by or applied to the edge zone (50) of the substructure (5b, 5a).

6. An electrochemically active element in accordance with claim 5, characterised in that the electrode layer applied to the edge zone (50) substantially consists of the same substance mixture as the substructure.

7. A method for the manufacture of a substructure (5, 5a, 5b) in accordance with any of claims 1 to 4, characterised in that at least one slurry (10) is prepared from a powder mixture (11) and a liquid (12, L); in that the or a first slurry is poured onto a mould (2, 3, 4) absorbent with respect to the liquid and is solidified to form a uniformly thick layer (5, 5'); in that optionally a further layer (5") is applied to the solidified layer (5') with a second or a further slurry; in that the intermediate product produced in this manner is dried, removed from the mould and finally sintered,

with the powder mixture including sinterable particles and organic components as pore forming materials and binding agents which go into a volatile form during sintering, and with the liquid, which in particular mainly consists of water, forming a suspension medium for the powder mixture together with at least one additive.

8. A method in accordance with claim 7, characterised in that the absorbent mould (3, 4) consists of a porous material (30), in particular gypsum; or in that the absorbent mould (2) is formed from an apparatus which comprises an extraction device (21, 22, 23, 24) having an inserted micro-filter film (20).

9. A method in accordance with claim 7 or 8, characterised in that cellulose fibres (60), graphite platelets, synthetic resin balls (61) or a mixture of all three or of two each of the said substances are used as the pore forming materials, with preferably cellulose fibres and/or a mixture of cellulose fibres and synthetic resin balls being used.

10. A method in accordance with any of claims 7 to 9, characterised in that the mould (3) is set into a vibration (36) during the pouring on of the slurry (10).

DATED this 14th day of March 2002.

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Fig.1

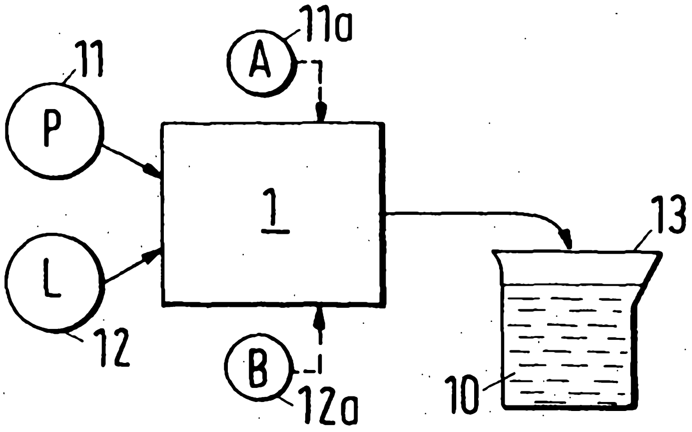



Fig.2

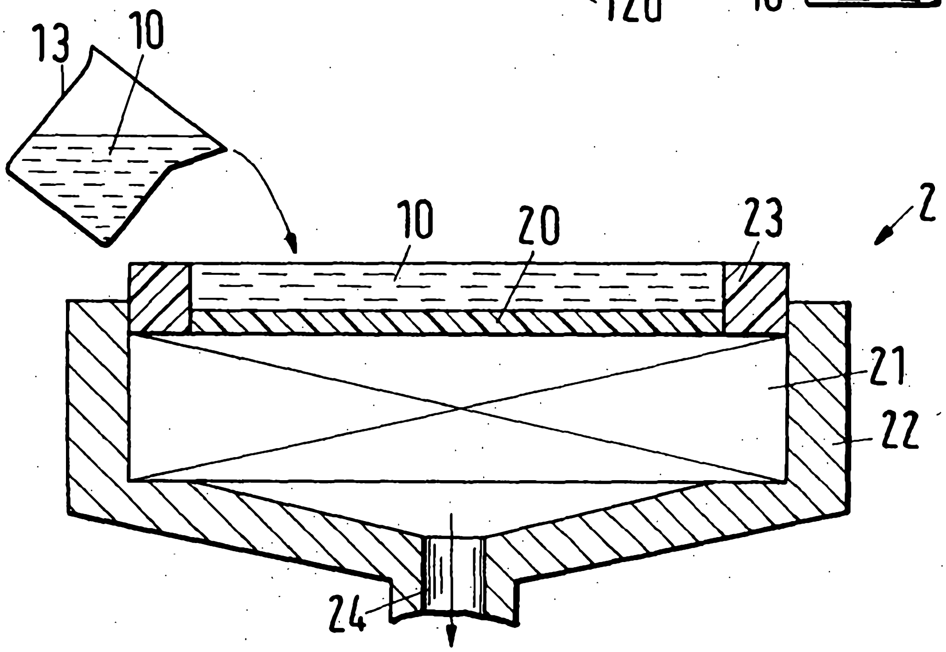



Fig.3

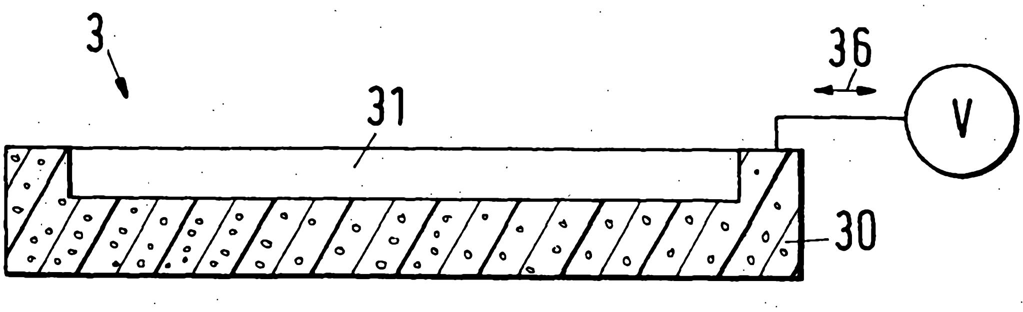



Fig.4

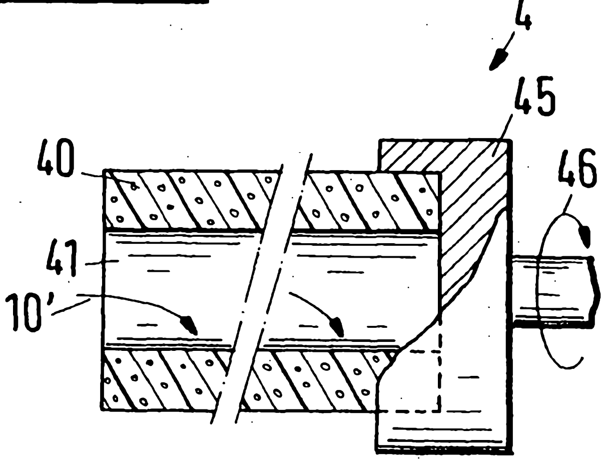


Fig.5

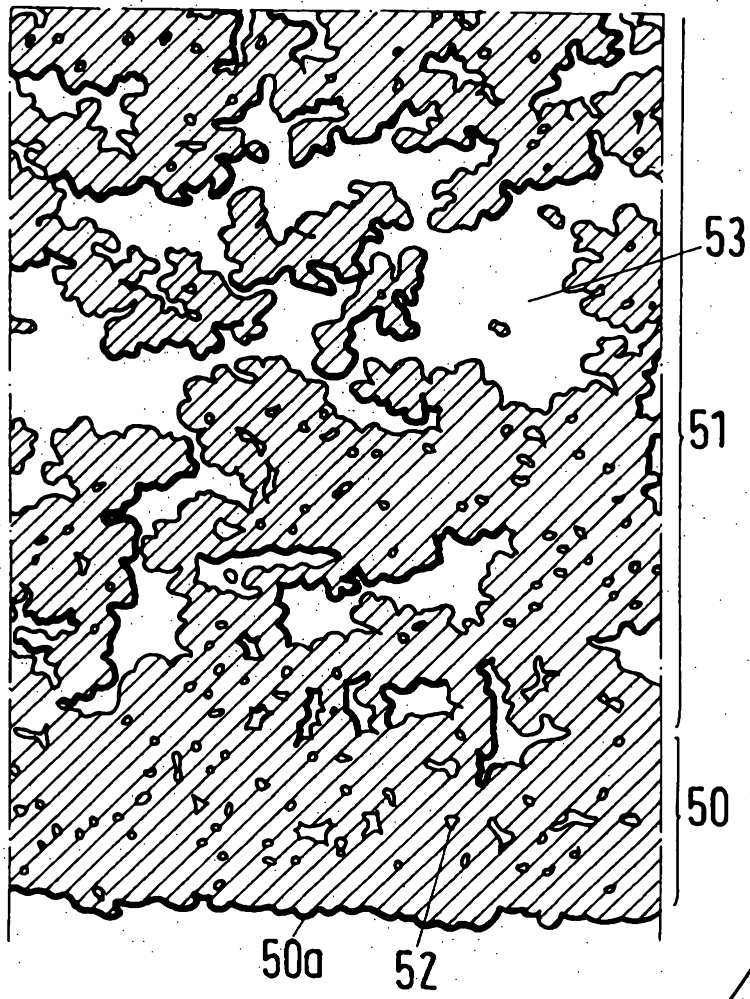



Fig.6

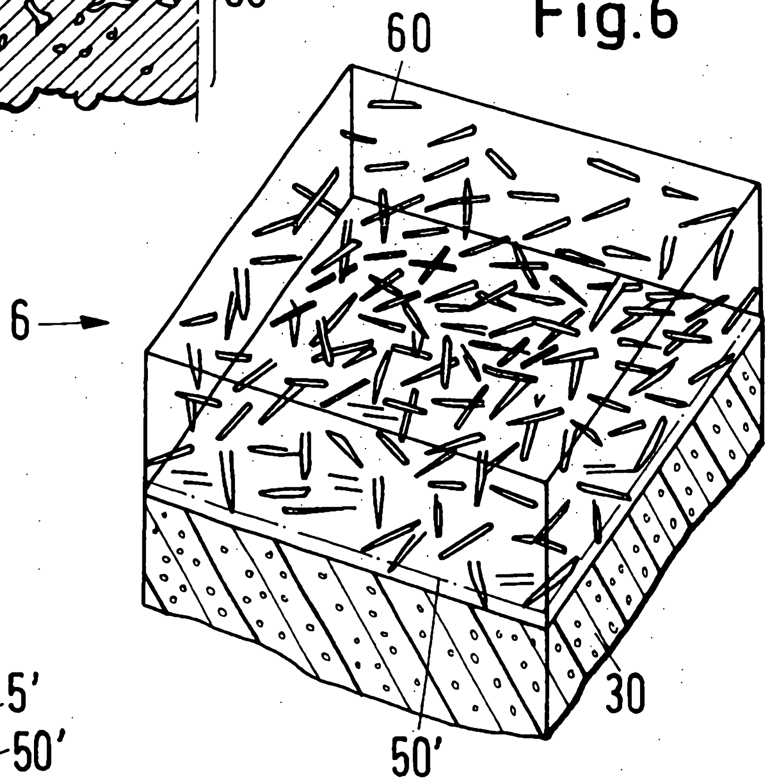



Fig.7

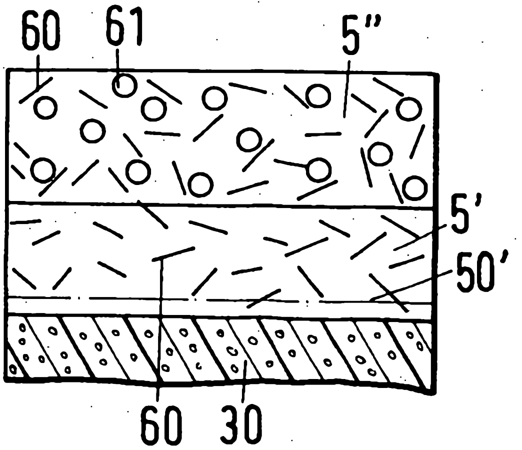
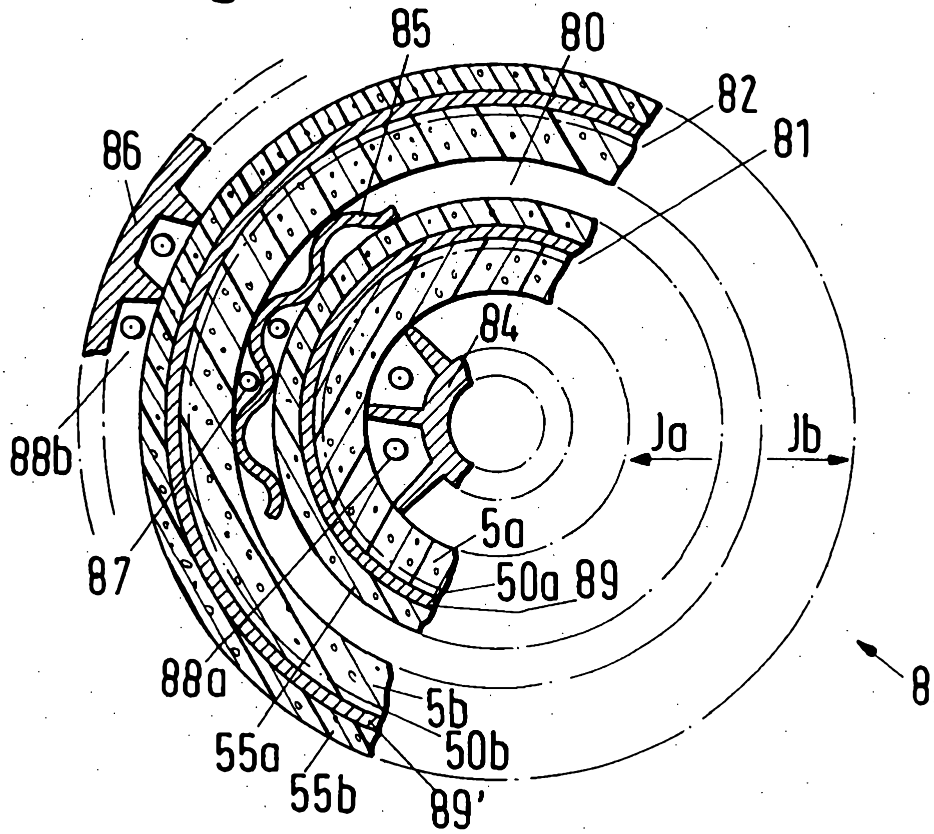


Fig.8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82
81
86
84
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Ja
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87
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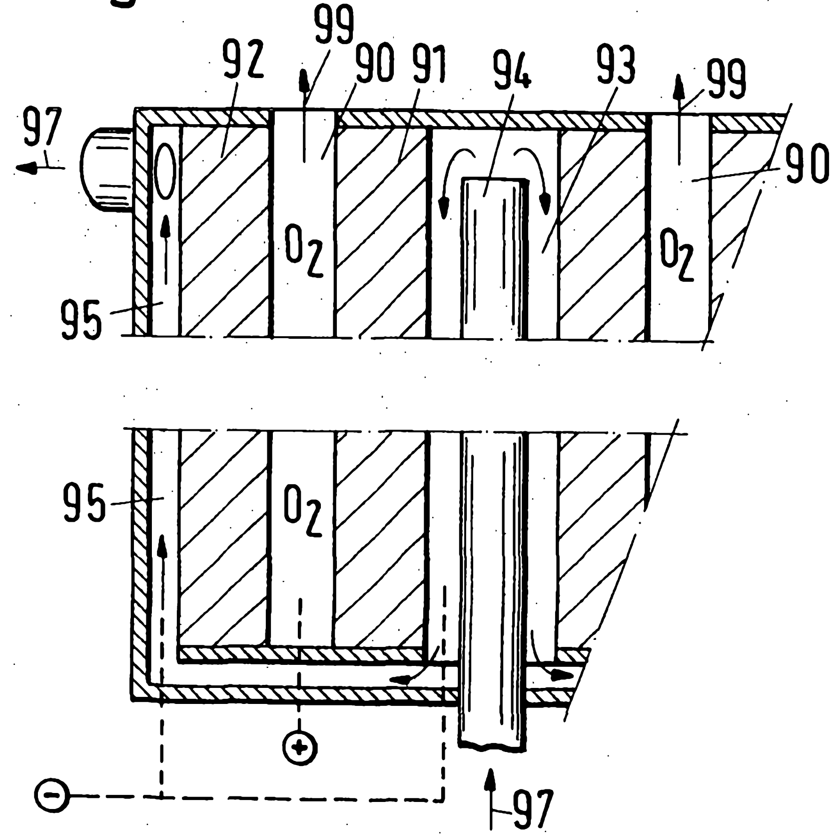
89
88a
8
5b
50b
55a
55b
89'

Fig.9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P/00/011 28/5/91
Regulation 3.2(2)

AUSTRALIA

*Patents Act 1990*

# COMPLETE SPECIFICATION
# STANDARD PATENT

Application Number:

Lodged:

Invention Title: **A POROUS, GAS PERMEABLE LAYER SUBSTRUCTURE FOR A THIN, GAS TIGHT LAYER FOR USE AS A FUNCTIONAL COMPONENT IN HIGH TEMPERATURE FUEL CELLS**

**The following statement is a full description of this invention, including the best method of performing it known to :- us**

P. 7145

01-1191

**Sulzer Hexis AG, CH-8400 Winterthur, Switzerland**

A porous, gas permeable layer substructure for a thin, gas tight layer for use as a functional component in high temperature fuel cells

The invention relates to a porous, gas permeable layer substructure for a thin, gas tight layer in accordance with the preamble of claim 1, which layer substructure is provided in particular for use as a functional component in high temperature fuel cells. The invention is also directed to an electrochemically active element for fuel cells and a method for the manufacture of the layer substructure.

Electrode reactions for the production of an electric current are carried out on electrochemically active membranes in high temperature fuel cells: namely a reducing reaction at the anode in which water or carbon dioxide are produced from hydrogen and carbon monoxide of a first gas flow; and an oxidising reaction at the cathode, in which ionic oxygen $O^{2-}$ is formed from molecular oxygen of a second gas flow while taking up electrons from a metallic conductor. The oxygen ions move through a solid electrolyte which separates the two electrodes in a gas tight manner and which is conductive for the oxygen ions at temperatures over 700°C. The reducing anode reaction with the oxygen ions takes place while discharging electrons to a further metallic conductor which makes a connection to an adjacent electrochemically active membrane or to a battery terminal. The electromechanically active membrane is a multi-layer system in whose manufacture each layer can be used as a carrier for an adjacent layer and this adjacent layer can be produced by means of thin film technology, for example a thermal spray method or using a screen printing method.

A high temperature fuel cell whose solid electrolyte is formed as part of a multi-layer membrane in the form of a thin layer is known from EP-A-0 788 175 (= P.6725). Such thin film electrolytes, which are 10 – 20 μm thick, can be applied to a porous carrier structure by means of a VPS method (vacuum plasma spray method). The carrier structure, which has to be permeable for the reactants, is made up of a base layer with large pores and a top layer with fine pores. It forms the substructure for the further layers of the electrochemically active element. The top layer can be made of a slurry and be rolled to form a thin film by means of a tape casting method, subsequently applied to the base layer and connected thereto by sintering.

In a preferred form, the carrier structure also has an electrochemical function as an electrode and an electric function as a good conductor in addition to its mechanical function as a carrier. The material for the cathode layer can be applied to the solid electrolyte layer by means of a screen printing method and using a slurry. This material is subsequently further converted into a functional layer by sintering.

It is the object of the invention to provide a porous, gas permeable substructure for a thin, gas tight layer, for example, for the above-named purpose. Such a substructure should in particular be usable as a carrier for an electrode layer of a high temperature fuel cell. This object is satisfied by the layer substructure defined in claim 1.

The porous, gas permeable layer substructure for a thin, gas tight layer can be used in particular as a functional component in high temperature fuel cells. This layer substructure has a smooth surface which is suitable for an application of the gas tight layer or of a multi-layer system comprising the gas tight layer, with the application being carried out by means of a screen printing method or other coating methods. The smooth surface is formed by a compacted edge zone. The edge zone and a carrier structure adjacent to this are made from a uniform substance mixture of sinterable particles. The porosity of the carrier structure is greater than 30 volume percent, preferably greater than 40 volume percent. The pore size of the edge zone is smaller than 10 μm, preferably smaller than 3 μm.

The dependent claims 2 to 4 relate to advantageous embodiments of the substructure for a layer or layers of the invention. An electrochemically active element is the subject of claims 5 and 6. Claims 7 to 10 relate to a method for the manufacture of a substructure of the invention.

The invention is explained in the following with reference to the drawings. There are shown:

Fig. 1 a preparation method for a slurry which is provided for the manufacture of the layer substructure shown in schematic form;

Fig. 2 a first mould for the method of the invention;

Figs. 3, 4 a second and a third mould;

Fig. 5 a cross-section through the product of the method of the invention, drawn in accordance with a photograph taken by means of raster electronic microscopy;

Fig. 6 an illustration of the spatial distribution of fibres which are included in a slurry used for the method of the invention;

Fig. 7 a schematically represented cross-section through a cast plate which comprises two layers;

Fig. 8 a cross-section through a fuel cell including two concentric tubes; and

Fig. 9 a longitudinal section through an oxygen generator which has substantially the same design as the fuel cell of Fig. 8.

For the manufacture of a layer substructure of the invention a slurry 10 is prepared from a powder mixture 11 containing sinterable particles and from a liquid 12: see Fig. 1. The powder mixture 11 includes, in addition to the sinterable particles, organic components which are provided as pore forming materials and as binding agents and which go into a volatile form during a sintering process in which they evaporate from the product largely free of residues. The liquid 12, which is advantageously mainly made of water, forms a suspension medium L for the particles of the powder mixtures 11 together with at least one additive. The slurry 10 is advantageously homogenised in a ball mill 1. Individual components 11a or 12a provided for the slurry can suffer losses in quality by the milling procedure. These components – in solid form A or liquid form B – are advantageously added to the mixture only towards the end of the milling procedure. A quantity required for a further method step is measured from the slurry 10 prepared in this way, in which solid particles are suspended in the liquid L using a vessel 13, which can for example be a syringe.

The further method step for the manufacture of the layer substructure of the invention is shown in Fig. 2. The slurry 10 is poured or sprayed from the vessel 13 onto a mould 2 which can absorb the liquid L and is thereby solidified into a uniformly thick layer. The mould 2 consists in the example shown of a micro-filter film 20, of a carrier structure 21, which is for example a strainer, of a wall 22 and of a frame 23, which can be made, for example, of plastic. A vacuum can be generated in the carrier structure 21 via an extraction connection 24 and the liquid L is partly extracted from the slurry 10 under the effect of said vacuum. Stretched polytetrafluoroethylene can, for example, be used as the micro-filter film 20.

When pouring the slurry into the trough, which is formed by the micro-filter film 20 and the frame 23, a layer is produced which solidifies due to the extraction of the liquid L. The intermediate product produced in this way is dried, removed from the mould and finally sintered. The product is suitable as a porous, gas permeable substructure for a thin, gas tight layer. The surface separated from the micro-filter film 20 is formed as smooth; it is suitable for an application of the gas tight layer or a multi-layer system comprising the gas tight layer. The material for the gas tight layer can be applied by means of a screen printing method or other coating methods. The smooth surface is formed by a compacted edge zone. The edge zone and a carrier structure adjacent to this consist of a uniform substance mixture. The carrier structure has a pore size, that is a medium pore diameter, which is substantially larger than the pore size of the edge zone. The porosity of the carrier structure is larger than 30 volume percent, preferably larger than 40 volume percent. The pore size of the edge zone is smaller than 10 μm, preferably smaller than 3 μm.

The layer substructure of the invention can also be made with simpler means, namely with a mould 3 which consists of a plate 30 made of gypsum with a trough-like recess 31: see Fig. 3. Instead of gypsum, another absorbent material, for example a porous plastic, can also be used with which a mould can be made whose recess 31 has a sufficiently smooth surface. In order to spread the slurry 10 uniformly into the recess 31 and in order to promote the formation of an edge zone, the mould 3 can be connected to a vibrator 35 which acts on the mould 3, for example, by an ultrasound vibration 36.

A cylindrical layer substructure can also be made with a gypsum tube 40 which can be placed onto a rotatable holder 45: see Fig. 4. The slurry 10 is injected or sprayed uniformly (arrows 10') onto the inner surface 41 of the tube lumens. The slurry is distributed uniformly due to the centrifugal force generated by a rotation 46 so that a tube with homogenous wall thickness is produced.

Fig. 5 shows a cross-section through a product 5 which has been made in accordance with the invention with the gypsum mould 3 of Fig. 3. It is drawn according to a photograph obtained by means of raster electron microscopy. A smooth surface 50a is formed by an edge zone 50 which includes small, partly closed pores 52. A carrier structure 51 adjacent to the edge zone 50 is substantially more porous. Pores 53 of the carrier structure 51 form a communicating pore space. The porosity of the edge zone 50 is less than 30 volume percent, preferably smaller than 10 volume percent. The thickness of the edge zone 50 is smaller than 100 μm, preferably smaller than 30 μm.

The large pores 53 of the carrier structure 51 have been produced by means of pore forming materials which go into a volatile form during sintering. Fig. 6 shows an illustration of the spatial distribution 6 of fibrous pore forming materials 60 which are included in a slurry 10 used for the method of the invention. An absorbent substrate 30 absorbs liquid L from the slurry 10. Fine particles of the slurry 10 are carried to the surface of the substrate 30 with the liquid L under the supporting effect of gravity where a compacted edge zone 50 is formed whose inner boundary is indicated by the chain dotted line 50'. The fibrous pore forming materials 60 have a lower density than the sinterable particles of the powder mixture 11. The edge zone can therefore be additionally enlarged by means of a vibration (cf. Fig. 3) due to the buoyancy forces acting on the pore forming materials 60.

Fig. 7 shows a schematically illustrated cross-section through a cast plate which comprises two layers 5', 5". A further layer 5" has been applied with a second slurry to the first layer 5' with fibrous pore forming materials 60, with spherical pore forming materials 61 also being added to the second slurry in addition to fibrous ones. A larger porosity is obtained for the second layer 5" than for the first. During sintering, the layers combine to form a cohesive structure.

Fig. 8 shows a cross-section through a fuel cell 8 which comprises two electrochemically active elements in the form of concentric tubes 81 and 82. A first gas flow 87 with reducing reactants is guided in an annular gap 80 between the two tubes 81, 82. A second gas flow, which includes molecular oxygen and which is formed from two branch flows 88a and 88b, is led over the inner surface of the tube 81 or over the outer surface of the tube 82 respectively. Metallic conductors 84, 85 and 86 serve as tube 82 respectively. Metallic conductors 84, 85 and 86 serve as collectors.

The tubes 81 and 82 are electrochemically active elements, each with a respective layer substructure 5a or 5b according to the invention. Such an element forms a multi-layer system which comprises an anode layer, a gas tight solid electrolyte layer and a cathode layer. The electrode layers, that is either the anode or the cathode layer, are applied to the edge zone 50 of the substructure 5a or 5b respectively; or the edge zones 50 themselves have the function of electrode layers. In the event that an additional electrode layer is applied to the edge zone 50, it is advantageous if the substructure 5a or 5b is substantially made of the same substance mixture as the electrode layer. In the inner tube 81, the substructure 5a of the invention is formed as a cathode on which a solid electrolyte layer 89 is applied, and an anode layer 55a on this; in the outer tube 82, the substructure 5b of the invention is formed as an anode on which a solid electrolyte layer 89' is applied, and an cathode layer 55a on this. The arrows Ja and Jb indicate the directions of the electric currents which are produced in the fuel cell 8.

A high temperature fuel cell having planar cells is disclosed in the above-mentioned EP-A-0 788 175. The electrochemically active elements of these cells can likewise be made with the layer substructure of the invention, with moulds being used in accordance with Figures 2 and 3.

Fig. 9 shows a longitudinal section through an oxygen generator 9 which has substantially the same design as the fuel cell 8 of Fig. 8 and which also works at high temperatures. The oxygen generator 9 comprises two electrochemically active elements 91, 92 and annular gap spaces 90, 93 and 95, in which collectors (not shown) – corresponding to the collectors 84, 85 and 86 in Fig. 8 – are arranged. Heated air 97 is fed into the inner annular gap space 93 via a central tube 94 and further guided from there into the outer annular gap space 95. An electric potential is applied (indicated by plus and minus terminals) between the annular gap space 90 and the annular gap spaces 93 and 95. Oxygen ions are transported through the solid electrolyte layers of the two elements 91 and 92, discharged in the annular gap space 90 and released as molecular oxygen. Pure oxygen $O_2$ (arrow 99) can thus be gained from air 97 in the annular gap space 90.

The layer substructure of the invention can also be used, in addition to fuel cells and oxygen generators, as functional components for a high temperature electrolysis apparatus in which hydrogen and oxygen are generated electrolytically from water vapour.

The structure illustrated in Fig. 5 and to be understood as an example, has been made with a slurry whose composition is suitable for the manufacture of an anode substructure and which is characterised by the following formula:

- 175 g nickel oxide NiO, whose particles have a mean diameter $d_{50}$ of 3 µm (50% by weight of the particles have a diameter which is smaller than $d_{50}$).

- 75 g zirconium oxide $ZrO_2$ which is stabilised with yttrium Y (YSZ); $d_{50}$ around 0.6 µm.

- 20 g water.

- 3 g dispersing agent which is already used in known ceramic processing methods (a polycarbonic acid with the brand name "Dispex A40" of the company of Prochem AG).
- 50 g binding agent (polyvinyl acetate "Vinapas®" EZ W 36).
- 10 g pore forming material in the form of cellulose (from deal, fibre length 20 – 150 µm.

Slurry preparation: water, dispersing agent, NiO and YSZ powder are crushed and dispersed on a ball mill with zirconium oxide milling balls (diameter 20 mm, weight ratio to milling material 2 : 1) for 16 hours. The cellulose fibres are subsequently added and dispersed for a further 2 hours. Finally, the binding agent is added and homogenised for 2 hours.

When used as an anode, the nickel oxide is reduced to nickel; the porosity increases in this process.

When a cathode layer is being made, a mixture is used for the sinterable particles which comprises a perovskite (e.g. $La_xSr_{1-x}MnO_3$) and YSZ (around 50% by weight each).

In addition to cellulose fibres, graphite platelets, synthetic resin balls or a mixture of all three or two each of the above substances can be used as pore forming materials. Preferably, however, cellulose fibres and/or a mixture of cellulose fibres and synthetic resin balls can be used.

In a so-called ASE cell (anode supported electrolyte cell), the carrier structure is located at the side of the reducing fuel gas ($H_2$, CO), i.e. at the anode side. In the manufacture of the ASE cell, the functional layers are applied onto the layer substructure of the invention by a coating method in the order anode, electrolyte and cathode. This multi-layer plate has a periphery which is exposed to an environment containing molecular oxygen during a current producing operation of the fuel cell. The material of the porous layer substructure, which consists largely of nickel, has the property that it adopts an oxidised or a reduced state depending on the environment at the operating temperature of the fuel cell. The periphery of the multi-layer plate must therefore be provided with a barrier which inhibits or prevents the transport of molecular oxygen from the surrounding environment into the layer substructure. Otherwise, the ASE cell, whose layer substructure is in the reduced state during operation, is changed by a topical oxidation in the edge region of the periphery such that damaging cracks occur. The layer substructure, which is manufactured by means of the mould shown in Fig. 3, is advantageously also given a compacted zone at its periphery with the method of the invention. This zone, which extends over the whole height of the layer substructure, has the advantage that it represents a barrier against the transport of molecular oxygen. The pores still present can be sealed with an additional means.

Claims

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A porous, gas permeable layer substructure (5; 5a, 5b) for a thin, gas impervious layer (89), in particular for use as a functional component in high temperature fuel cells (8), which layer substructure has a smooth surface (50a) which is suitable for an application of the gas impervious layer or a multi-layer system including the gas impervious layer by means of a screen printing method or other coating methods, characterised in that the smooth surface is formed by a compacted edge zone (50); in that the edge zone and a carrier structure (51) adjacent to this are made from a uniform substance mixture consisting of sinterable particles; in that the porosity of the carrier structure is greater than 30 volume percent, preferably greater than 40 volume percent; and in that the pore size of the edge zone is smaller than 10 μm, preferably smaller than 3 μm.

2. A substructure for a layer in accordance with claim 1, characterised in that the porosity of the edge zone (50) is smaller than 30 volume percent, preferably smaller than 10 volume percent; and in that the thickness of the edge zone is smaller than 100 μm, preferably smaller than 30 μm.

3. A substructure for a layer in accordance with claim 1 or claim 2, characterised in that it is made up of a first layer (5') including the edge zone (50) and at least one second porous layer (5"), with the layers being sintered to form a cohesive structure and the second layer having a greater porosity than the first.

4. A substructure for a layer in accordance with any of claims 1 to 3, characterised in that it is formed in plate shape (5) or in that it has a tubular shape (81, 82), with the edge zone preferably forming the outer surface of the tube (81, 82).

5. An electrochemically active element (81, 82; 91, 92), in particular a high temperature fuel cell (8) or an oxygen generator (9) having a substructure (5a, 5b) in accordance with any of claims 1 to 4 and a multi-layer system which comprises an anode layer (55a, 50b), a gas impervious solid electrolyte layer (89) and a cathode layer (50a, 55b), with each of the electrode layers, that is either the anode layer (50b) or the cathode layer (50a), being formed by or applied to the edge zone (50) of the substructure (5b, 5a).

6. An electrochemically active element in accordance with claim 5, characterised in that the electrode layer applied to the edge zone (50) substantially consists of the same substance mixture as the substructure.

7. A method for the manufacture of a substructure (5, 5a, 5b) in accordance with any of claims 1 to 4, characterised in that at least one slurry (10) is prepared from a powder mixture (11) and a liquid (12, L); in that the or a first slurry is poured onto a mould (2, 3, 4) absorbent with respect to the liquid and is solidified to form a uniformly thick layer (5, 5'); in that optionally a further layer (5") is applied to the solidified layer (5') with a second or a further slurry; in that the intermediate product produced in this manner is dried, removed from the mould and finally sintered,

with the powder mixture including sinterable particles and organic components as pore forming materials and binding agents which go into a volatile form during sintering, and with the liquid, which in particular mainly consists of water, forming a suspension medium for the powder mixture together with at least one additive.

8. A method in accordance with claim 7, characterised in that the absorbent mould (3, 4) consists of a porous material (30), in particular gypsum; or in that the absorbent mould (2) is formed from an apparatus which comprises an extraction device (21, 22, 23, 24) having an inserted micro-filter film (20).

9. A method in accordance with claim 7 or 8, characterised in that cellulose fibres (60), graphite platelets, synthetic resin balls (61) or a mixture of all three or of two each of the said substances are used as the pore forming materials, with preferably cellulose fibres and/or a mixture of cellulose fibres and synthetic resin balls being used.

10. A method in accordance with any of claims 7 to 9, characterised in that the mould (3) is set into a vibration (36) during the pouring on of the slurry (10).

DATED this 14th day of March 2002.

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Fig.1

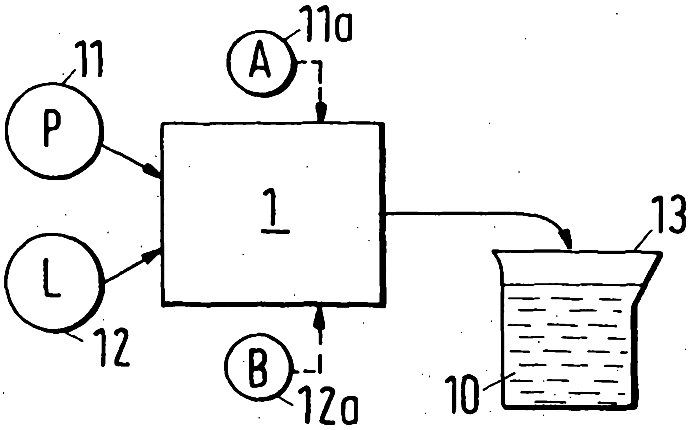



Fig.2

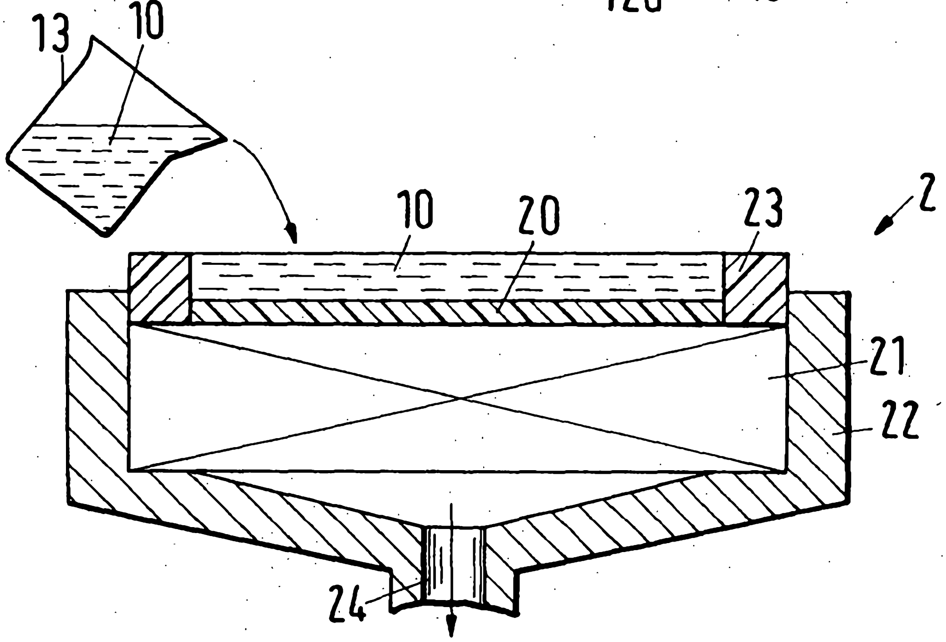



Fig.3

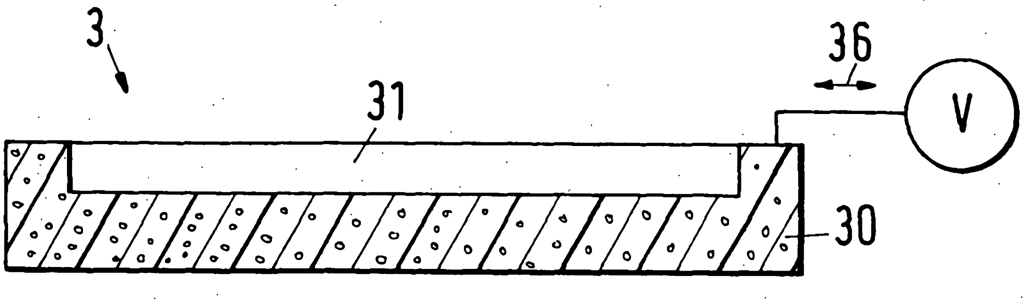



Fig.4

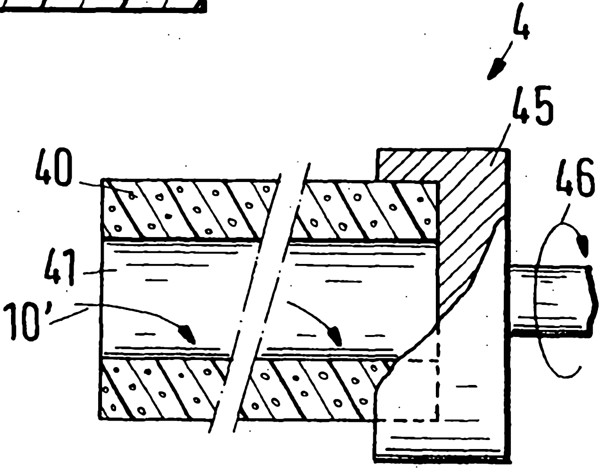


Fig.5

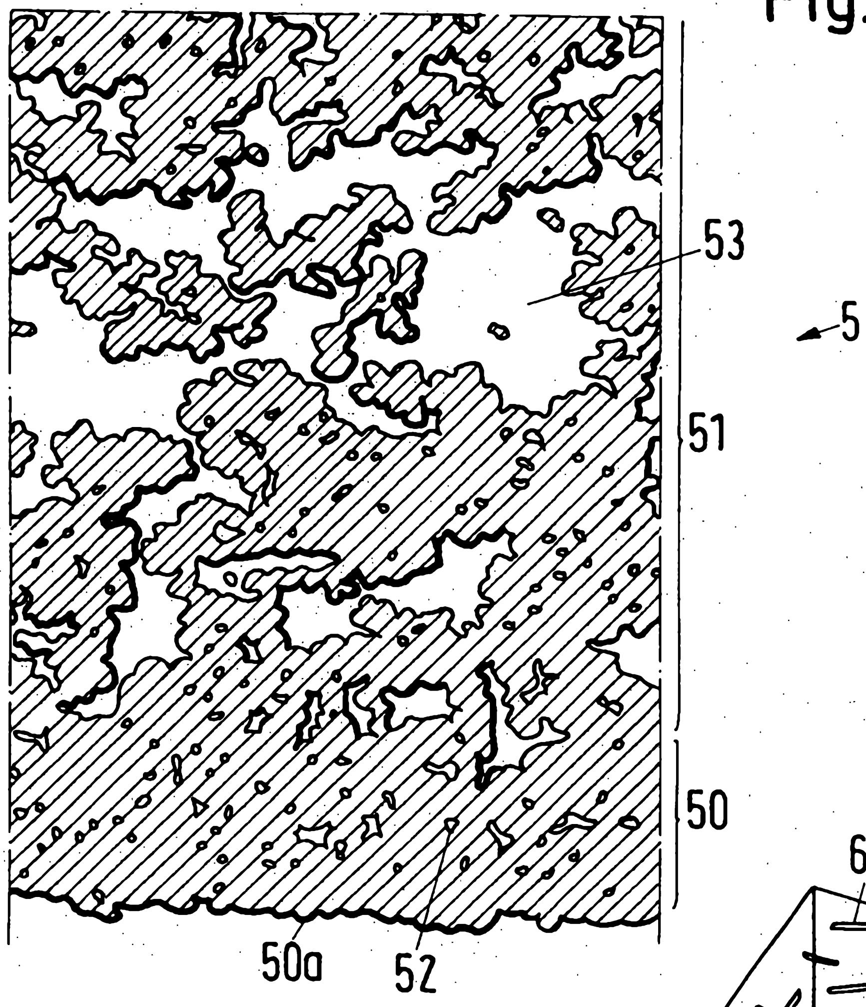



Fig.6

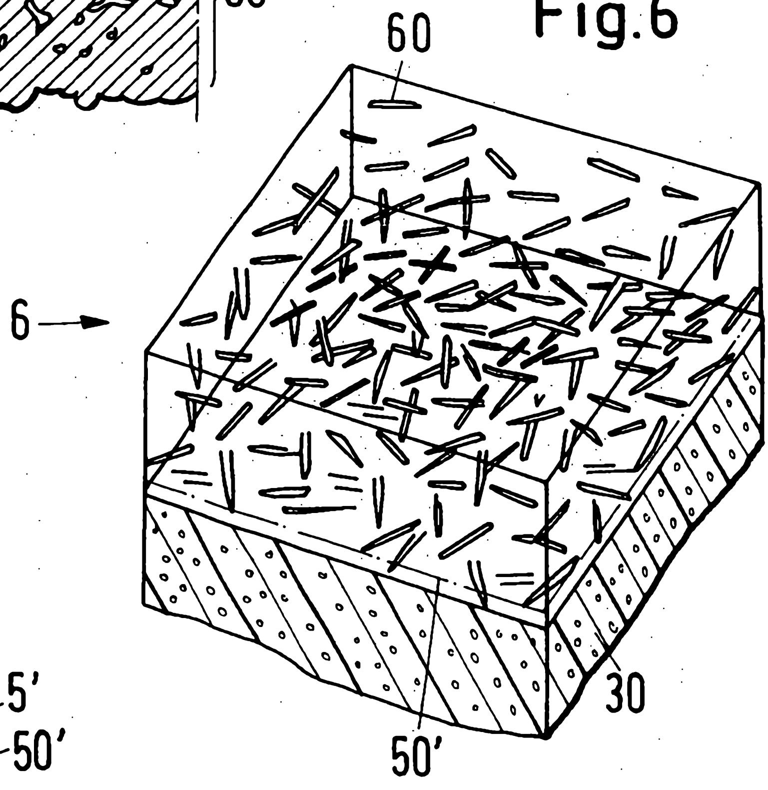



Fig.7

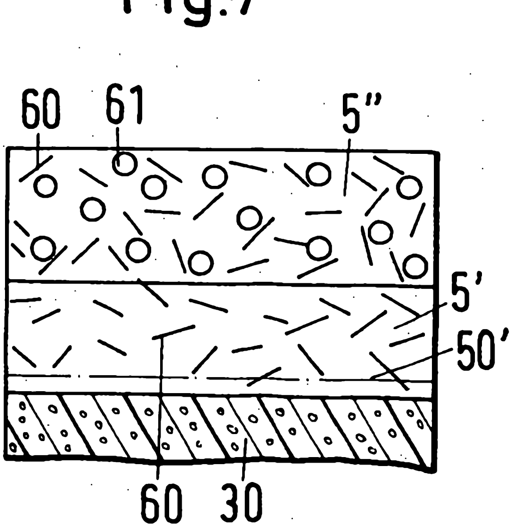
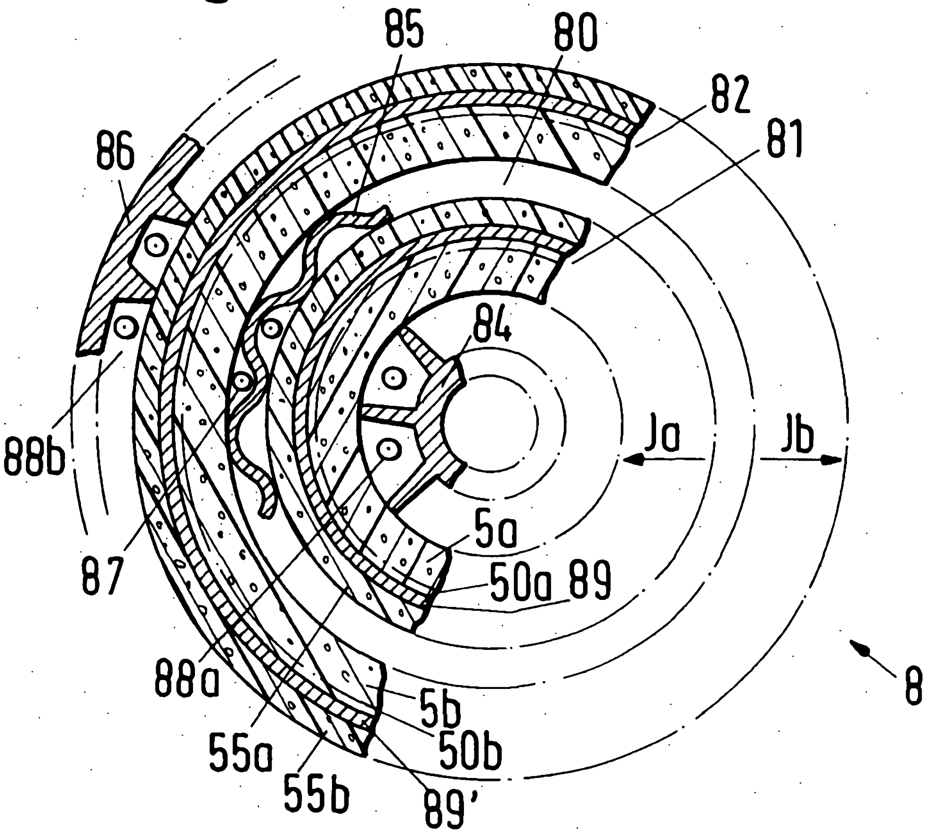


Fig.8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55b
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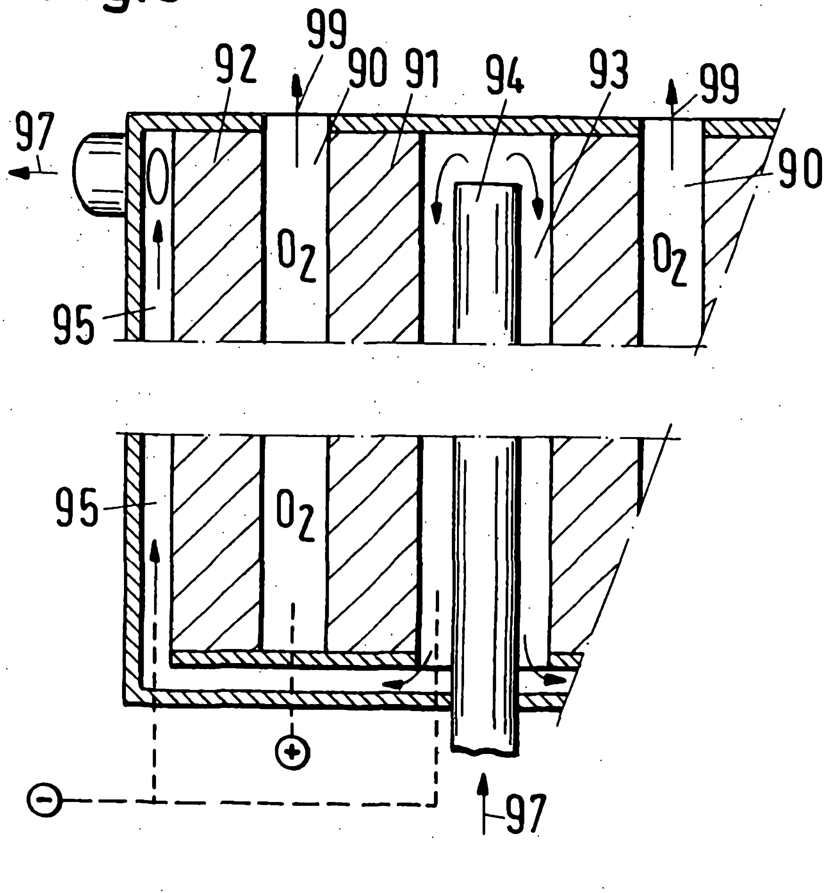
Fig.9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