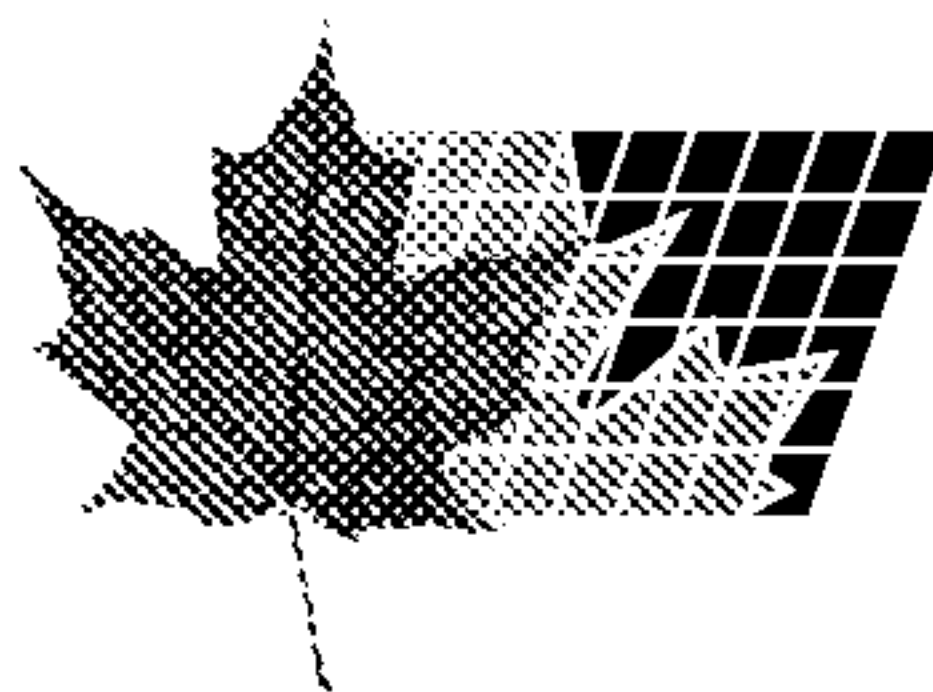




(72) RENNEBECK, KLAUS, DE

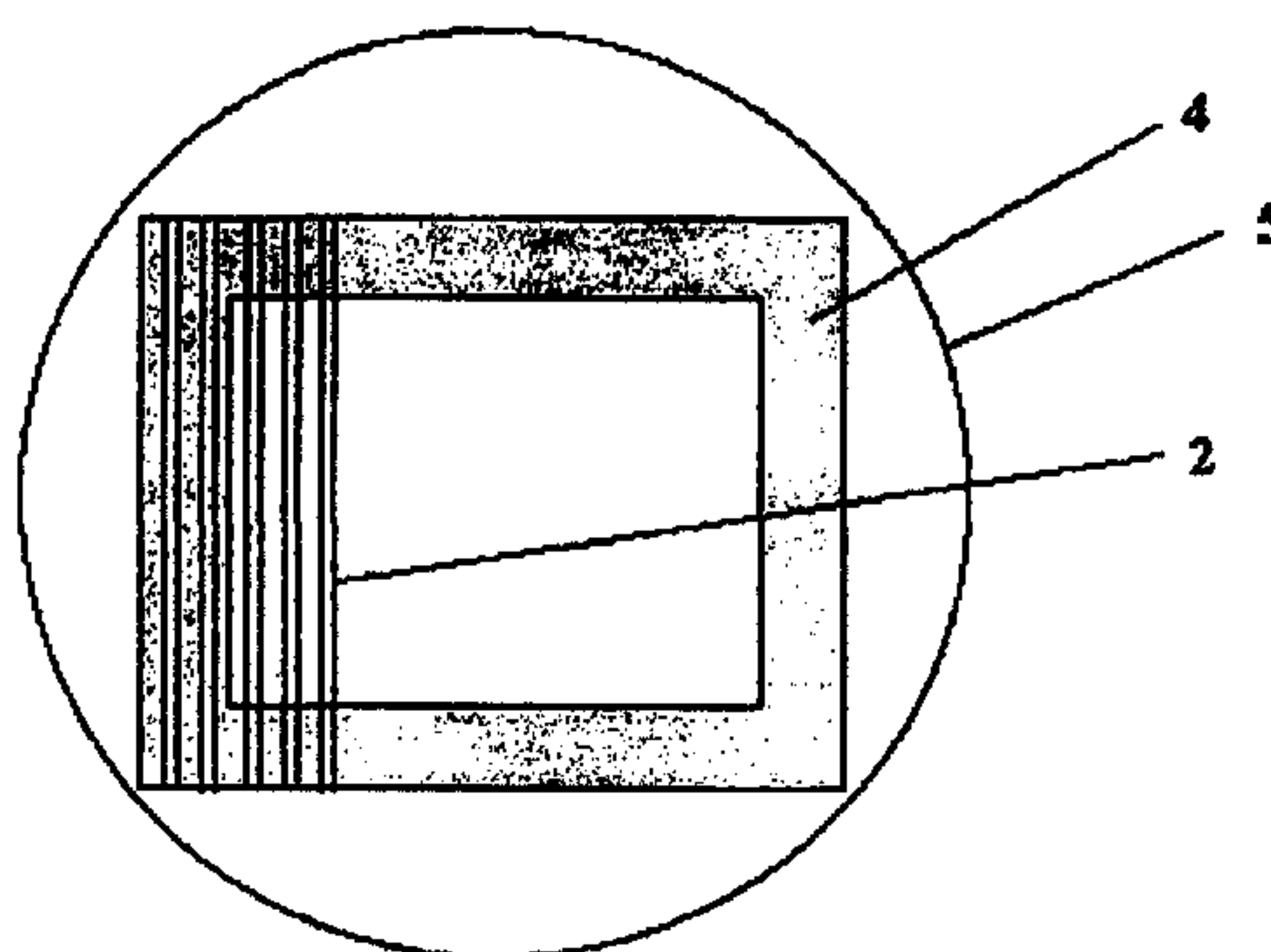
(71) RENNEBECK, KLAUS, DE

(51) Int.Cl.⁶ H01M 8/10, H01M 8/24, B05B 1/14, H01M 8/04

(30) 1997/12/28 (197 57 786.5) DE

(54) **UNITE DE PILE A COMBUSTIBLE**

(54) **FUEL CELL UNIT**



(57) L'invention concerne une unité de pile à combustible servant à produire du courant continu par conversion d'énergie chimique, avec un électrolyte qui porte une anode et une cathode séparément l'une de l'autre. L'unité de pile à combustible présente un électrolyte matriciel à microfibres creuses (2). Lesdites microfibres creuses font entre 0,01 et 50 μm d'épaisseur et ont un diamètre équivalent d'environ 0,05 à 280 μm . Les microfibres creuses se présentent soit sous forme de structures à base de filaments ou de fils continus, les extrémités (3) des microfibres creuses étant reliées de manière indéformable et mises à nues au moins partiellement pour permettre l'accès au lumen des fibres creuses ou sont disposées sous forme de structures de fibres empilées ou de fils de fibres empilées, les extrémités des microfibres creuses (3) étant liées de manière indéformable. L'invention concerne en outre un empilement de piles à combustible (1) composé de plusieurs unités de piles à combustible de ce type, ainsi que l'utilisation d'une unité de pile à combustible de ce type.

(57) The invention relates to a fuel cell unit for producing a continuous current by converting chemical energy, using an electrolyte which supports an anode and a cathode separately from each other. Said fuel cell unit has a self-supporting hollow microfibre-matrix electrolyte (2). Said hollow microfibres have a wall thickness of approximately 0.01 to 50 μm and an equivalent diameter of approximately 0.05 to 280 μm . The hollow microfibres are arranged in the form of bonded filament or filament yarn fabrics, in which case the ends (3) of the hollow microfibre are bonded in such a way that they are dimensionally stable and are left at least partially free to allow access to the lumen of the hollow fibre, or bonded staple fibre or staple fibre yarn fabrics, in which case the hollow microfibre ends (3) are bound in such a way that they are dimensionally stable. The invention also relates to a fuel cell stack (1) made up of several fuel cell units of this type, and to the use of a fuel cell unit of this type.



PCT
WELTORGANISATION FÜR GEISTIGES EIGENTUM
Internationales Büro
INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE
INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

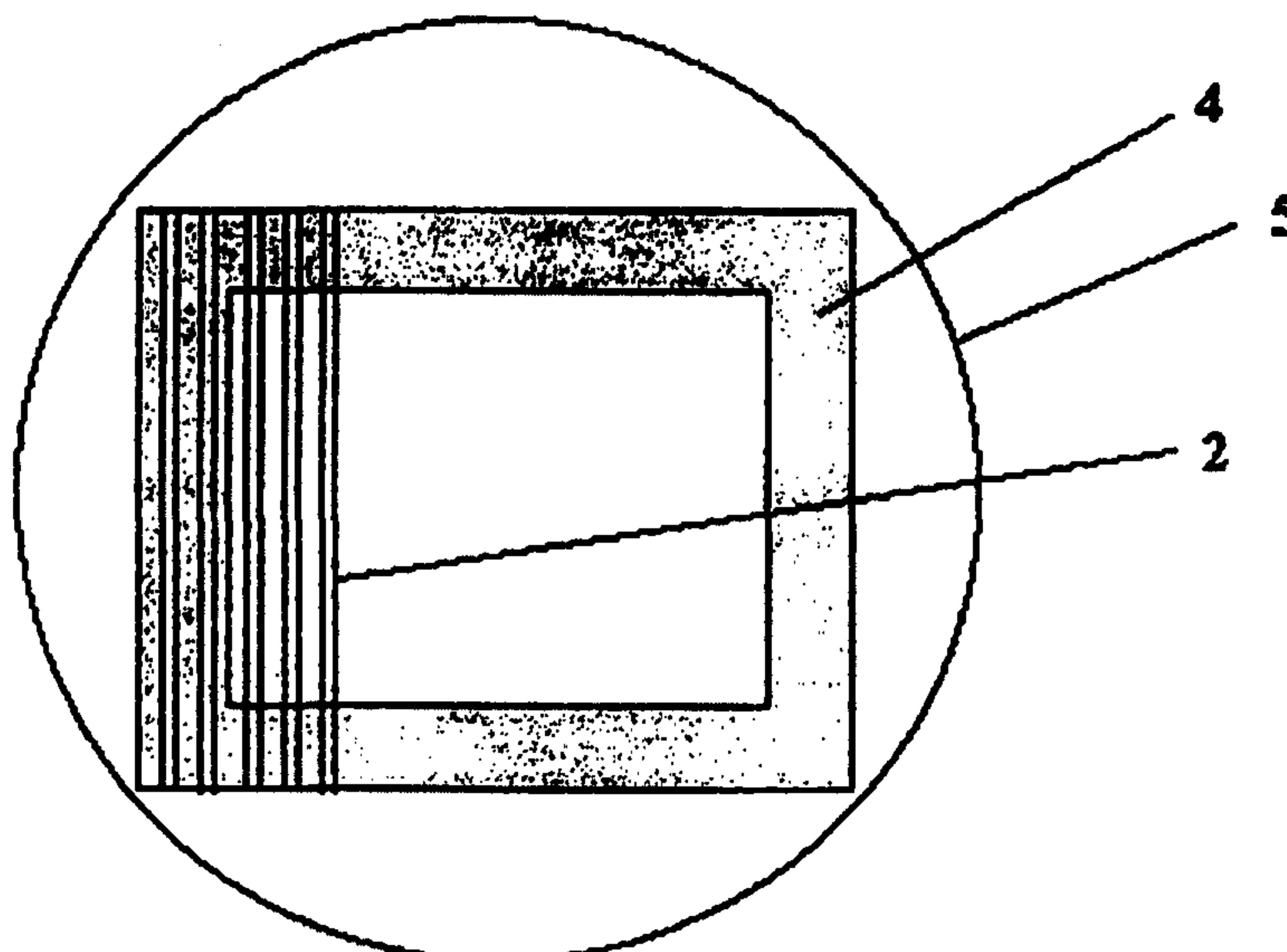
(51) Internationale Patentklassifikation ⁶ : H01M 8/00	A2	(11) Internationale Veröffentlichungsnummer: WO 99/34464 (43) Internationales Veröffentlichungsdatum: 8. Juli 1999 (08.07.99)
(21) Internationales Aktenzeichen: PCT/EP98/08432 (22) Internationales Anmeldedatum: 23. Dezember 1998 (23.12.98) (30) Prioritätsdaten: 197 57 786.5 28. Dezember 1997 (28.12.97) DE (71)(72) Anmelder und Erfinder: RENNEBECK, Klaus [DE/DE]; Blumenstrasse 16, D-73240 Wendlingen (DE). (74) Anwälte: HAGEMANN, Heinrich usw.; Hagemann, Braun & Held, Postfach 86 03 29, D-81630 München (DE).	(81) Bestimmungsstaaten: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO Patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Veröffentlicht <i>Ohne internationalen Recherchenbericht und erneut zu veröffentlichen nach Erhalt des Berichts.</i>	

(54) Title: FUEL CELL UNIT

(54) Bezeichnung: BRENNSTOFFZELLENEINHEIT

(57) Abstract

The invention relates to a fuel cell unit for producing a continuous current by converting chemical energy, using an electrolyte which supports an anode and a cathode separately from each other. Said fuel cell unit has a self-supporting hollow microfibre-matrix electrolyte (2). Said hollow microfibres have a wall thickness of approximately 0.01 to 50 μm and an equivalent diameter of approximately 0.05 to 280 μm . The hollow microfibres are arranged in the form of bonded filament or filament yarn fabrics, in which case the ends (3) of the hollow microfibre are bonded in such a way that they are dimensionally stable and are left at least partially free to allow access to the lumen of the hollow fibre, or bonded staple fibre or staple fibre yarn fabrics, in which case the hollow microfibre ends (3) are bound in such a way that they are dimensionally stable. The invention also relates to a fuel cell stack (1) made up of several fuel cell units of this type, and to the use of a fuel cell unit of this type.



Fuel cell unit

The present invention relates to a fuel cell unit for the direct current generation by transformation of chemical energy with an electrolyte, which carries an anode and cathode separately from one another. The invention furthermore relates to a fuel cell stack which is composed of several such fuel cell units as well as to the use of such a fuel cell unit.

Fuel cells, as is generally known, are used for the current generation, or more accurately the transformation of chemical into electrical energy. With this, on the anode, while releasing hydrogen ions, electrons are given off which charge the anode negatively. Accordingly, two reactions take place on the surface layers of the solid electrolyte, one on the anode and one on the cathode, which together form the principle of the fuel cell reaction. From the anode (plus pole) the electrode current is passed via a current consumer to the cathode (minus pole). Simultaneously with the generating of the flow of electrons from the anode to the cathode, the emission of the reaction product, e.g. water or water vapour (aqua destillata or condensate emission) takes place from the fuel cell. To operate a fuel cell a supply of fuel or working material is required which may consist, for example, of hydrogen or a hydrogen carrier. The fuel must be conveyed to the catalytic anode, the oxygen or oxygen carrier, i.e. the oxidising agent, to the surface of the cathode which is separated from the anode by the electrolyte. With an ideal electrolyte of a fuel cell a current generation takes place at a voltage of 1,23 Volt.

An example of a fuel cell where the anode and cathode are plate-shaped and are arranged on either side of an also plate-shaped electrolyte, has been disclosed in the US-A-5 418 079. Such plate-shaped electrolytes have the disadvantage that they must have a relatively great thickness so as to ensure an adequate stability for the handling. However, since with the increase in thickness of the electrolyte

also the diffusion path of the ions becomes longer, which leads to a higher starting temperature of the fuel cell, such plate electrolytes are only to a limited extent suitable for use in fuel cells. In addition such fuel cells have at a given volume an only small active surface for the electrochemical reaction.

The object of the present invention is, therefore, to indicate a fuel cell unit which in the smallest possible space has a large reactive surface, which is easy to manufacture and displays a high flexibility with regard to its use.

According to the invention this object is achieved by a fuel cell unit according to claim 1, as well as by a fuel cell stack which is composed of several such fuel cell units.

The fuel cell unit according to the invention for the direct current generation by transformation of chemical energy with an electrolyte, which carries an anode and cathode separately from one another, accordingly has a micro-hollow fibre matrix electrolyte, wherein the micro-hollow fibres have a wall thickness of approx. 0,01 to 50 μm and an equivalent outside diameter of approx. 0,05 to 280 μm , wherein the micro-hollow fibres are arranged either in the form of filament or filament yarn lays, wherein the micro-hollow fibre ends are bound in a form-stable manner and are at least partially exposed for the access to the hollow fibre lumen, or are arranged in the form of staple fibre or staple fibre yarn lays, wherein the micro-hollow fibres ends are bound in a form-stable manner.

By the fuel cell unit according to the invention in a small space a high active surface, e.g. approx. 11.000 cm^2 per cm^3 fuel cell volume, can be obtained. Understood under an equivalent diameter, as is generally known, for geometrical structures with an only approximately circular cross-section is the diameter of that fictitious circle, the area of which is equal to the cross-sectional area of the geometrical structure. In the present text filament lays refers to layers of fibres with which at least some of the fibres have one or more twists, whereas the

fibres in staple fibre lays extend without twists. Yarn lays are characterised in that several fibres or filaments are twisted together.

Seeing that according to the invention the solid electrolyte has the form of hollow fibres, i.e. a capillary or hollow profile, small wall thicknesses of the electrolyte can be realised without mechanical stability problems. Another advantage of the present invention consists in that micro-hollow fibres with the mentioned dimensions have textile properties and for this reason can easily be deformed without breaking. The inside and outside surfaces of the micro-hollow fibres are activated for their function as anode or cathode. The type of activation depends on the materials chosen for the micro-hollow fibres. For example, an activation by means of a suitable coating is possible.

The wall thickness of the micro-hollow fibres preferably lies between approx. 0,05 and 10 μm , in particular between approx. 0,05 and 5 μm . In this case the equivalent outside diameter of the micro-hollow fibres preferably lies between approx. 1 and 100 μm , in particular between approx. 2 and 25 μm . The concrete choice of the suitable diameters and wall thicknesses must be made in dependence on the materials used. The indicated lower values for wall thickness and diameter are determined in particular by the possibilities of the manufacture.

According to a preferred embodiment of the invention the lays are arranged in the form of a discus plate, wherein the micro-hollow fibre ends are bound-in in such a way that a stable, self-supporting discus plate ring is formed, at the outer annular peripheral surface of which the open micro-hollow fibres ends are exposed. The discus plate can, seen in cross-section, constitute a flat plate or may also have the shape of a layer of corrugated cardboard. The micro-hollow fibres forming the lay preferably have an equivalent diameter of approx. 0,5 to 100 μm as well as a length of preferably approx. 50 mm to 1000 mm. In this way, in a volume which corresponds to approx. 3 to 5 sheets of DIN A4 an electrolyte surface of approx. 1 m^2 can be obtained.

Seeing that the micro-hollow fibres are open at both ends, their length corresponds to the length of the lumen or channel, onto the inside surface of which either the anode or cathode is applied. Particularly preferred is a length of approx. 300 mm. The chosen length of the micro-hollow fibres preferably corresponds to the diameter of the discus plate ring. The micro-hollow fibre length can also amount to a multiple of the discus plate diameter by a turning around or bending over of the micro-hollow fibres. For the thickness of the ring values between approx. 1 mm and 35 mm have proved particularly suitable so that the function of the discus plate ring as form stabiliser will be fulfilled. The height of the discus plate ring preferably is approx. 0,5 mm to 15 mm. This height suffices to accommodate several micro-hollow fibre layers above one another. Such a ring is suitable for a stack of several fuel cell units.

Alternatively the lays may also be arranged in the form of a polygon, in particular a rectangle, wherein the hollow fibre ends are bound-in in such a way that a stable, self-supporting, polygonal, in particular rectangular, frame is formed, at the outer peripheral surface of which the open micro-hollow fibre ends are exposed. The individual micro-hollow fibres may in this case be arranged either parallel to one another or crossing one another, wherein the length of the micro-hollow fibres preferably corresponds approximately to the length or width respectively of the frame.

Preferably, the micro-hollow fibres are made of polymer materials, metal, ceramic and/or textile materials. However, also any other suitable materials may be used. The materials may be oxidic as well as non-oxidic. If non-fluorinated polymer materials are used for making the micro-hollow fibres, then the activation may take place, for example, by sulphonation.

Within the framework of the present invention especially those micro-hollow fibres have proved suitable that are indicated in the international application WO

97/26225, the disclosure of which is to be included here in full. These are micro-hollow fibres of a ceramic material or the corresponding green products. When in this connection mention is made of a "ceramic material", this is to be understood in the widest sense. It is a collective name for materials composed of inorganic and mainly non-metallic compounds or elements, which in particular comprise more than 30% by volume crystallised materials. In this connection reference is made to Römpp Chemie Lexikon, 9th edition, volume 3, 1990, p. 2193 to 2195. Preferably the ceramic micro-hollow fibres consist of an oxidic, silicatic, nitridic and/or carbidic ceramic material. Particularly preferred are such ceramic hollow fibres on the basis of aluminium oxide, calcium phosphate (apatite) or associated phosphates, porcelain- or cordierite-like compositions, mullite, titanium oxide, titanates, zirconium oxide, zirconium silicate, zirconates, spinels, emerald, sapphire, corundum, nitrides or carbides of silicon or other chemical elements or their mixtures. As doping agents the substances known in the ceramics industry, such as MgO , CaO , ZrO_2 , ZrSiO_4 , Y_2O_3 and others or their precursors may be added to the inorganic main constituents.

To manufacture these micro-hollow fibres preferably an emulsion, dispersion and/or suspension, which contains the precursor of a ceramic material and a binding agent that can be removed by means of heat, are formed in the known manner into green micro-hollow fibres and the binding agent is removed by means of heat. Alternatively the dispersion may be applied onto a core of an organic compact fibre, in which case subsequently both the core and the binding agent are removed by means of heat. The dispersion may contain changing quantities, e.g. up to 95% by mass, preferably approximately 40 to 70% by mass dispersion medium. A dispersion medium may also fall away when the binding agent is, for example, thermoplastic and can be melted without appreciable decomposition into a low-viscosity compound.

As the abovementioned ceramic precursors in particular the following can be used: clay minerals, in particular kaolin, illite, montmorillite, metal hydroxides such as aluminium hydroxide, mixed metal hydroxides/oxides, such as AlOOH ,

mixed metal oxides/halogenides, metal oxides such as BeO, MgO, Al₂O₃, ZrO₂ and ThO₂, metal nitrates such as Al(NO₃)₃, metal alcoholates, in particular aluminium alcoholates such as Al(iPrO)₃, Al(*sec*-BuO)₃, magnesium-alumino-silicates, feldspars, zeolites, böhmrites or mixtures of two or more of the aforementioned materials.

Regarding the choice of the binding agent that can be removed by means of heat, there exists no critical limitation within the framework of the invention. However, it is preferred that the binding agent is film-forming. It may, for example, be urea, polyvinyl alcohol, wax, gelatine, agar, protein, saccharide. Optionally, in addition organic ancillary agents, such as binding agents, suspension agents, defoaming agents and preservatives may be used. The mixture of the precursor of the ceramic material and the binding agent that can be removed by heat occurs in the form of a dispersion, which term is to be understood in its widest sense. It may, in particular, be emulsions and suspensions which regularly occur in the form of a paste. For the choice of the dispersion medium a high degree of freedom exists. Generally it will be water. However, it is also possible to use as liquid an organic solvent, such as an alcohol or acetone, optionally also mixed with water. Particularly advantageous here are so-called sol-gel processes, e.g. on the basis of the already mentioned polyvinyl alcohol.

It must be emphasised that already the abovementioned green product of the micro-hollow fibres can also in principle be used within the framework of the present invention. In this case it is particularly advantageous to subsequently sulphonate the green product of the micro-hollow fibres. This results in that the desirable proton conductivity is improved.

To manufacture the abovementioned micro-hollow fibres as well as the corresponding green products, in particular within the framework of a spinning process, the procedure is such that the dispersion is put into a feeding tank or pressure vessel of a spinning device, the dispersion is conveyed flowing at a

temperature of approx. 20 to 400°C through the spinning device and pressed through nozzle ring openings or nozzle profile openings. The partial flows produced in the area of the nozzle openings are split in the middle by cores or by devices for blowing in a gas, and the partial flows are solidified into green micro-hollow fibres by heating, by radiation or by feeding in a reaction partner and are then optionally burned to dense micro-hollow fibres. Further details can be noted from the already mentioned international application WO 97/26225.

It is furthermore possible to use as micro-hollow fibres the hairs of the pelts of those animal types, whose pelt hairs have an inside lumen. The pelt hairs, because of their protein constituents, have a high proton conductivity and are, therefore, suitable for the fuel cell unit according to the invention.

Depending on the intended application as well as the fuel that is to be used, the fuel cell unit may be a PEM, DM and SO fuel cell unit. As is already known the abbreviations "PEM", "DM" and "SO" stand for "Proton Exchange Membrane", "Direct Membrane" and "Solid Oxide" respectively. For PEM fuel cell units in particular the green polymer products of the micro-hollow fibres are suitable, whereas the micro-hollow fibres in the burned state are particularly suitable for the manufacture of SO fuel cell units. As starting material for high temperature fuel cells, zirconium dioxide and in particular zirconium can be recommended, as this metal has a high absorption capacity for water. Furthermore the materials PEEK (polyetheretherketone) as well as Victrex® have proved suitable within the framework of the use according to the invention. By means of a suitable choice of material any type of fuel cell can, therefore, be produced.

The anode may be applied on the inside lumen surfaces of the micro-hollow fibres as well as on the outside peripheral surfaces of the micro-hollow fibres. However, for application reasons further details of which will be given further on, it is preferred that the anode is provided on the outside periphery of the electrolyte and the cathode on the inside lumen surface of the micro-hollow fibres in question.

According to a particularly preferred embodiment the fuel cell unit is provided with a microwave screening cage. This serves to screen off the rays of a microwave heating which frequently is used to bring the fuel cell to its starting temperature, i.e. the temperature at which the electrochemical reaction takes place.

To avoid short-circuits between the individual micro-hollow fibres that form the matrix electrolyte, a short-circuit protection in the form of helical fibres with non-activated surface may be provided, which are wound around the micro-hollow fibres and are fixed to the ends thereof.

The fuel cell units according to the invention may be combined to form a fuel cell stack, by which the capacity of the individual fuel cell units can be multiplied practically at will. In such a stack the individual fuel cell units may be embedded or cast in such a way that a stable, self-supporting frame is formed. This frame may have any shape, e.g. a discus plate ring as already explained in the foregoing.

The individual fuel cell units of the fuel cell stack according to the invention may be corrugated or web plate shaped. In this form the individual fuel cell units can easily be placed on top of one another.

The fuel cell stack according to the invention may comprise at least one fuel cell unit with non-activated electrode surfaces as heat exchanger and/or air filter. This is a special advantage of the construction of the fuel cell unit according to the invention with a matrix electrolyte of micro-hollow fibres. The heat exchanger and/or air filter may, as a matter of fact, consist of matrix electrolyte filaments of the same material and morphology, the only difference being that their surfaces are not activated so that the chemical reaction desired for the current generation cannot take place on them. The fuel cell unit or fuel cell unit stack according to the invention can in this way be manufactured particularly easily and in a few steps, wherein several elements (fuel cell units, heat

exchanger, air filter etc.) are first made as identical elements and subsequently a splitting up of the functions takes place by a specific activation of individual micro-hollow fibres.

The matrix electrolytes of micro-hollow fibres according to the invention can be made into the respective individual fuel cell units by twining (for example roping or braiding). The micro-hollow fibres with non-activated surface, which serve as heat exchanger and/or air filter, are preferably applied on the micro-hollow fibres acting as electrolyte in an electrically insulated manner in such a way that they are wound helically around the micro-hollow fibres. The insulated helical winding is preferably connected at the matrix ends of the fuel cell units to the micro-hollow fibres acting as electrolyte in a solid and non-detachable manner, wherein the anode surfaces are not reduced. In this way the outside surface of the micro-hollow fibres of the matrix acting as electrolyte remains exposed for the fuel access. At the same time the insulated helix acts as a textile contact and touching protection for the outside surfaces of the hollow fibres of the matrix electrolyte. From the miniature individual fuel cells, series circuits can be produced in lays and stacks.

To make the fuel cell stack, the individual micro-hollow fibres may be made into a flat article with random orientation or as a lay according to a scheme. It is possible that complete stacks are used as heat exchangers, in which case the micro-hollow fibres of these stacks have non-activated surfaces. By stacking the individual stacks, they may be made into stable modules in which stacks with activated and stacks with non-activated micro-hollow fibres may alternate. The non-activated stacks may furthermore act as a cooler, recuperator of the fuel or a pre-heater. When the individual fuel cell stacks have a discus plate shape, the stacking will result in operating cylinders that are easy to handle.

For the operation as a fuel cell, micro-hollow fibres with wall thicknesses between approx. 0,05 μm and 40 μm and with an outside diameter of approx. 0,1 μm to approx. 50 μm have proved particularly suitable. In individual cases

the lumen diameter may also amount up to 100 μm . To obtain these small diameter and wall thicknesses, preferably the manufacturing process described in the foregoing is used.

When using the fuel cell unit according to the invention or the fuel cell stack according to the invention for the direct current generation by transformation of the chemical energy released during the oxidation of a fuel, the material flows of the fuel and of the oxidising agent preferably are guided in cross-current. This means that one of the material flows is guided perpendicular to the plane of the filament or stack fibre lay and the other parallel to this plane. This is in contrast to the operation of the known fuel cells, where the electrolytes are either plate shaped or in the form of flat films and the material flows of the fuel and oxidising agent are accordingly guided parallel or opposite parallel along the plate planes. With the known fuel cells this arrangement leads to the disadvantage that, for example, the concentration of the oxygen in the oxidising agent becomes less the further the oxidising agent has moved along the plate plane. In contrast thereto, when using the fuel cell unit or fuel cell stack according to the invention the oxidising agent, because of the cross current mode of operation, can be fed into both ends of the respective micro-hollow fibres. This means that along the entire micro-hollow fibre length a substantially constant oxygen concentration is present, as a result of which the capacity of the fuel cell unit can be kept constant.

Hydrogen-containing fuels have proved particularly suitable for operating the fuel cell stack according to the invention because of their high reactivity.

The reaction products preferably are used for the conditioning, heating, cooling and/or moisturising of the fuel cell unit or other connected sequences. The connected sequence may be, for example, a connected fuel cell unit or an element independent of the fuel cell. In this manner the fuel is utilised several times and a particularly economical process can be realised. In the sense of the multiple use of the fuel the reaction product of the oxidation, e.g. water, can also

be passed on for further use in an air conditioning system, for example in a motor vehicle.

To start the fuel cell reaction generally a higher temperature is required, which is also called the starting temperature of the fuel cell. This starting temperature can be obtained according to the invention by passing a heating medium through the fuel cell stack in one of the branches of the cross currents. The heating media may be, for example, the products of the electrochemical reaction.

The electrolyte starting temperature can be obtained by heating the fuel and/or the oxidising agent before feeding it into the fuel cell unit. The heat required to heat the fuel and/or the oxidising agent can be obtained, for example, by wetting zeolite. As is known, when they absorb water zeolites heat up to a temperature of $+70^{\circ}\text{C}$ to $+370^{\circ}\text{C}$. The zeolite wetting can in turn preferably take place with the products of the electrochemical reaction (aqua destillata).

The electrolyte starting temperature may also be obtained by wetting a metal hydride, in particular iron, titanium, magnesium hydride. Also for this wetting it is possible, of course, to use the end product of the electrochemical reaction.

Furthermore it is possible to obtain the starting temperature by a direct or indirect circulating of metal or barium hydroxide melts. In this connection barium hydroxide is particularly suitable, as it is liquid already at approx. 78°C and accordingly can be circulated as a liquid in the desired temperature range. The metal melt or barium hydroxide melt must, of course, be passed through separately from the material flows of the fuel and oxidising agent.

The electrolyte starting temperature can also be obtained by radiating the fuel cell unit with microwaves. In this case the fuel cell or the fuel cell stack and the housing must be made such that microwaves can pass through them, in which case the overall unit must be integrated in a microwave screening cage which in order to save weight preferably is made as a light construction. This form of

heating can also be used in combination with one of the other aforementioned heating methods. All mentioned heating methods have the advantage that they can be carried out without pressure, which is advantageous from the construction point of view.

A fuel cell quick-start can also be realised by an atmospheric catalyst burner, i.e. a gas-liquid burner. It is also possible to use the catalyst burner in combination with one or several of the aforementioned methods for bringing the fuel cell or fuel cells tack up to temperature.

Depending on the type of activation of the catalyst surface, this may take place both before the mounting or assembly of the fuel cell stack as well as after the commissioning of the fuel cell, for example for a touching up. The outside and inside surfaces of the micro-hollow fibres lumens may also act alternately as cathode or anode.

The spraying in of fuel preferably takes place through nozzles, the openings of which are shaped as micro-hollow fibre lumens that have a diameter of 0,1 μm to 100 μm and are provided lost in the cast or injection moulded parts of the nozzle. In this manner a particularly accurate metering of the fuel as well as a extremely fine distribution thereof is possible.

The fuel injection nozzle, the openings of which are shaped as micro-hollow fibre lumens that have a diameter of 0,1 μm to 100 μm and are provided lost in the cast or injection moulded parts of the nozzle, constitutes a considerable improvement of the previously known fuel injection nozzles. It is possible to manufacture this nozzle by the aforementioned method with a fluctuation range of the outside diameter of only approximately $\pm 6\%$. Nozzles with openings of the mentioned sizes and the indicated precision cannot, however, as usual be made by making holes in a metal blank by means of laser radiation seeing that this method entails a high degree of inaccuracy. To make the nozzle openings according to the invention it is better to place micro-hollow fibres lost in the

injection moulding parts or the casting mould parts of the nozzle before they are filled with the actual nozzle material, e.g. metal. The openings which act as nozzles may, for example, be produced in them after removal of the micro-hollow fibres with the aid of micro-wire, e.g. tungsten glow lamp wire. In this case the wire is pulled out of the extrusion pressing profile and in this way forms the spraying lumen.

In the following the invention will be explained in greater detail with reference to the attached drawings which are not given as a limitative example. In the drawings:

Figure 1 shows a first embodiment of a fuel cells tack according to the invention;

Figure 1a is a cross-section of Figure 1;

Figure 2 is a perspective view of a second embodiment of a fuel cell stack according to the invention;

Figure 3 is a diagrammatic view of the fuel cell stack of Figure 2, in which in particular the circuit of the fuel cell stack according to the invention is shown; and

Figure 3a is a cross-sectional view of Figure 3 in elevation.

In Figure 1 a fuel cell stack according to the invention is illustrated, which has been given the overall reference numeral 1. The fuel cell stack 1 is composed of micro-hollow fibres 2 which form the electrolyte and as a filament or staple fibre lay are formed into a flat article with random orientation or according to a fixed scheme. The solid electrolyte is present, therefore, in the form of a matrix.

The ends 3 of the individual micro-hollow fibres are open and are exposed on the outside periphery of a frame 4, which in this case is a rectangular frame. The frame 4 serves to stabilise the shape and preferably is made of an electrically insulating casting compound. In this case the ends 3 of the micro-hollow fibres 2 can during the manufacture of the fuel cell stack be cast into the frame.

However, also any other type of embedding of the micro-hollow fibres 2 into the frame 4 is possible, for example also just a loose embedding.

The fuel cell stacks according to the invention of the embodiment illustrated in Figure 1 can be stacked so that a compact, stable fuel cell square is produced. Around the individual stacks or stack of stacks a housing 5 is provided which, depending on the mechanical, thermal or chemical or process stresses on the individual components, may, for example, be made of plastic, metal, glass or ceramic. When microwave radiation is used to heat the fuel cell, a material must be used for the housing that allows this type of radiation to pass through. In this case, to protect the operator or user, a screening cage must be provided around the entire device including the microwave heating. Preferably the housing is made of a dielectric material, so that an electric insulation of the fuel cell stack is ensured.

The fuel cell stack according to the invention may be operated in the pressure as well as the vacuum mode. In the first case the housing 5 must be constructed suitable for the pressure in question. Here, for example, cylindrical pressure housings have proved particularly advantageous.

Figure 1a shows the embodiment of Figure 1 in cross-section. In the illustrated embodiment the micro-hollow fibres 2 are arranged parallel in one direction (in the Figures 1 and 1a for reasons of clarity only a few of the micro-hollow fibres 2 are shown). As already mentioned in the foregoing, they may however also be arranged crosswise to one another. The bottom 6 of the housing 5 may be constructed, for example, as a dished bottom so as to be able to withstand higher pressure conditions. For the pressure operation in addition a compressor 7 is required, as illustrated symbolically in Figure 1a.

In Figure 2 another embodiment of a fuel cell stack 1 according to the invention is illustrated, with which the frame 4 has the shape of a discus plate ring. The micro-hollow fibres 2, of which in Figure 2 for reasons of clarity only one individual one is shown partly, extend along the diameter of the discus plate, wherein the hollow fibre ends 3 are exposed at the lateral periphery of the ring.

As example for the dimensioning of such a stack the following values can be indicated:

- Diameter of the discus plate ring: 230 mm
- Height h of the discus plate ring 5 mm
- Thickness d of the discus plate ring: 35 mm
- Outside diameter of the micro-hollow fibres: 10 μ m

The active surface of the micro-hollow fibres may be made, in particular, of molecular screen, activated charcoal, graphite, aluminosilicate, zeolite or spongy materials as well as elements and compounds of the 8th sub-group.

Figure 3 shows in a perspective view a fuel cell stack 1 with a frame 4 in the form of a discus plate ring as illustrated in Figure 2. From this illustration it can be noted how the two electrodes 8, 9 of the fuel cell stack can be arranged on the dielectric frame 4. According to the illustrated mounting of the electrodes, by placing several fuel cell stacks next to one another, a series circuit can be produced, and by stacking them on top of one another a parallel circuit.

Figure 3a shows the fuel cell stack of Figure 3 in cross-section, wherein for greater clarity of the illustration only one micro-hollow fibre 2 is shown which extends into the frame 4. On the outside surface of the micro-hollow fibre 2 one of the two electrodes 10 of the micro-hollow fibre is located, which may be an anode or cathode. The electrode 10 of the micro-hollow fibre is in direct contact with the corresponding electrode 9 which is provided on the periphery of the frame. From the other of the two micro-hollow fibre electrodes (not illustrated),

which is provided on the inside surface of the micro-hollow fibre, a line leads out from the discus plate ring to the second electrode 8 of the discus plate ring.

When the anodes are arranged on the inside surfaces of the micro-hollow fibres, the product of the electrochemical reaction will occur on the outside surfaces of the fibres which form the cathode. In this case the cathode contact with the housing is obtained directly, and the oxidising agent or air is filtered through the layers of micro-hollow fibres.

The fuel cells stack according to the invention can be used among others as an atmospheric fuel cell with closed fuel supply and open elimination of the reaction product, e.g. water. Furthermore both the vacuum and pressure mode of operation can be used, the former of which is particularly suitable for use in a motor vehicle, where the wind caused by the travelling ensures the vacuum in the fuel cell stack. The individual micro-hollow fibres are self-supporting and because of their textile properties extremely flexible and resistant. Because of the thin wall thicknesses of the micro-hollow fibres low starting temperatures can be realised. The micro-hollow fibres according to the invention can be produced with an accuracy of $\pm 6\%$ with regard to the fluctuation of the outside diameter and the wall thickness, so that a constant mode of operation is ensured.

The injection nozzle described within the framework of the use of the fuel cell stack according to the invention is also suitable for use in other fields, in particular in connection with Otto carburettor engines or diesel engines, in Carnot cycle processes or other similar processes or machines.

* * *

1. Fuel cell unit for the direct current generation by transformation of chemical energy with an electrolyte, which carries an anode and cathode separately from one another, characterised in that
 - a) the electrolyte is a micro-hollow fibres matrix electrolyte,
 - b) the micro-hollow fibres (2) of the electrolyte have a wall thickness of approx. 0,01 to 50 μm and an equivalent outside diameter of approx. 0,05 to 280 μm ,
 - c) the micro-hollow fibres are arranged either in the form of filament or filament yarn lays, wherein the micro-hollow fibre ends (3) are bound in a form-stable manner and are at least partially exposed for the access to the hollow fibre lumen, or are arranged in the form of staple fibre or staple fibre yarn lays, wherein the micro-hollow fibres ends (3) are bound in a form-stable manner,

the lays being arranged in the form of a discus plate, wherein the micro-hollow fibre ends are bound-in in such a way that a stable, self-supporting discus plate ring is formed, at the outer annular peripheral surface of which the open micro-hollow fibre ends are exposed; or the lays being arranged in the form of a polygon, in particular a rectangle, wherein the hollow fibre ends are bound-in in such a way that a stable, self-supporting, polygonal, in particular rectangular, frame is formed, at the outer peripheral surface of which the open micro-hollow fibre ends are exposed.

AMENDED SHEET

2. Fuel cell unit according to claim 1, characterised in that the wall thickness of the micro-hollow fibres lies between approx. 0,05 and 10 μm , in particular between approx. 0,05 and 5 μm .
3. Fuel cell unit according to claim 1 or 2, characterised in that the equivalent outside diameter of the micro-hollow fibres lies between approx. 1 and 100 μm , in particular between approx. 2 and 25 μm .
- 10 4. Fuel cell unit according to at least one of the preceding claims, characterised in that the micro-hollow fibres (2) are made of polymer materials, metal, ceramic and/or textile materials.
5. Fuel cell unit according to at least one of the preceding claims, characterised in that the fuel cell unit is a PEM, DM or SO fuel cell unit.
6. Fuel cell unit according to at least one of the preceding claims, characterised in that the anode is provided on the inside lumen surface of the micro-hollow fibres (2).
- 20 7. Fuel cell unit according to at least one of the preceding claims 1 to 5, characterised in that the anode is provided on the outside peripheral surface of the micro-hollow fibres (2).
8. Fuel cell unit according to at least one of the preceding claims, characterised in that it is provided with a microwave screening cage.
9. Fuel cell unit according to at least one of the preceding claims, characterised in that a short-circuit protection in the form of helical fibres with non-activated surface is provided, which are wound around the micro-
30 hollow fibres and are fixed to the ends thereof.

10. Fuel cell stack (1) which contains several fuel cell units according to at least one of the preceding claims.
11. Fuel cell stack according to claim 10, characterised in that the individual fuel cell units are corrugated or web plate shaped.
12. Fuel cell stack according to claim 10 or 11, characterised in that it comprises at least one fuel cell unit with non-activated electrode surfaces as heat exchanger and/or air filter.

10

13. Use of at least one fuel cell unit or fuel cell stack according to any one of the preceding claims 1 to 12 for the direct current generation by transformation of the chemical energy released during the oxidation of a fuel, characterised in that the material flows of the fuel and of the oxidising agent are guided in cross-current.

14. Use according to claim 13, characterised in that a hydrogen-containing fuel is used.

20

15. Use according to claim 13 or 14, characterised in that the electrochemical oxidation products are used for the conditioning, heating, cooling and/or moisturising of the fuel cell unit or other connected sequences, in particular connected fuel cell unit sequences.

16. Use according to at least one of the claims 13 to 15, characterised in that the electrolyte starting temperature is obtained by passing a heating medium through the at least one fuel cell unit or the fuel cell stack in one of the branches of the cross currents.

30

17. Use according to at least one of the claims 13 to 15, characterised in that the electrolyte starting temperature is obtained by heating the fuel and/or the oxidising agent before feeding it into the fuel cell unit.

18. Use according to claim 16 or 17, characterised in that the heat required to heat the fuel, the oxidising agent or the heating medium is obtained by wetting zeolite.
19. Use according to claim 16, characterised in that the electrolyte starting temperature is obtained by wetting a metal hydride, in particular iron, titanium, magnesium hydride.
- 10 20. Use according to claim 18 or 19, characterised in that the end product of the electrochemical reaction is used for the wetting.
21. Use according to claim 16, characterised in that the electrolyte starting temperature is obtained by a direct or indirect circulating of metal or barium hydroxide melts.
22. Use according to at least one of the claims 13 to 21, characterised in that the electrolyte starting temperature is obtained by radiating the fuel cell unit with microwaves.
- 20 23. Use according to at least one of the claims 13 to 22, characterised in that the electrolyte starting temperature is obtained with an atmospheric catalyst burner.
24. Use according to at least one of the claims 13 to 23, characterised in that the spraying in of fuel takes place through nozzles, the openings of which are shaped as micro-hollow fibre lumens that have a diameter of 0,1 μm to 100 μm and are provided lost in the cast or injection moulded parts of the nozzle.

25. Fuel injection nozzle, in particular within the framework of the use according to claim 24, characterised in that the openings of the nozzle are shaped as micro-hollow fibre lumens that have a diameter of 0,1 μm to 100 μm and are provided lost in the cast or injection moulded parts of the nozzle.

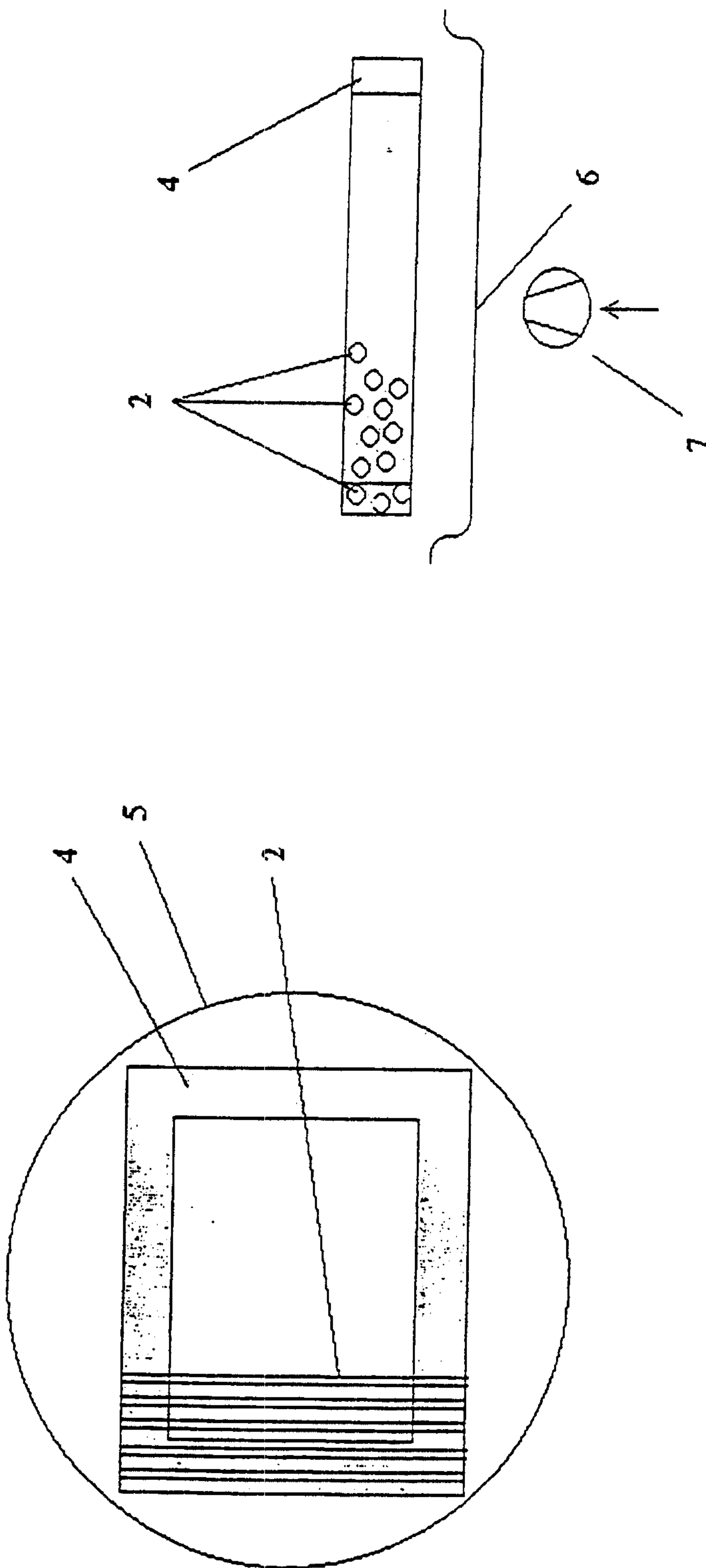


Fig. 1a

Fig. 1

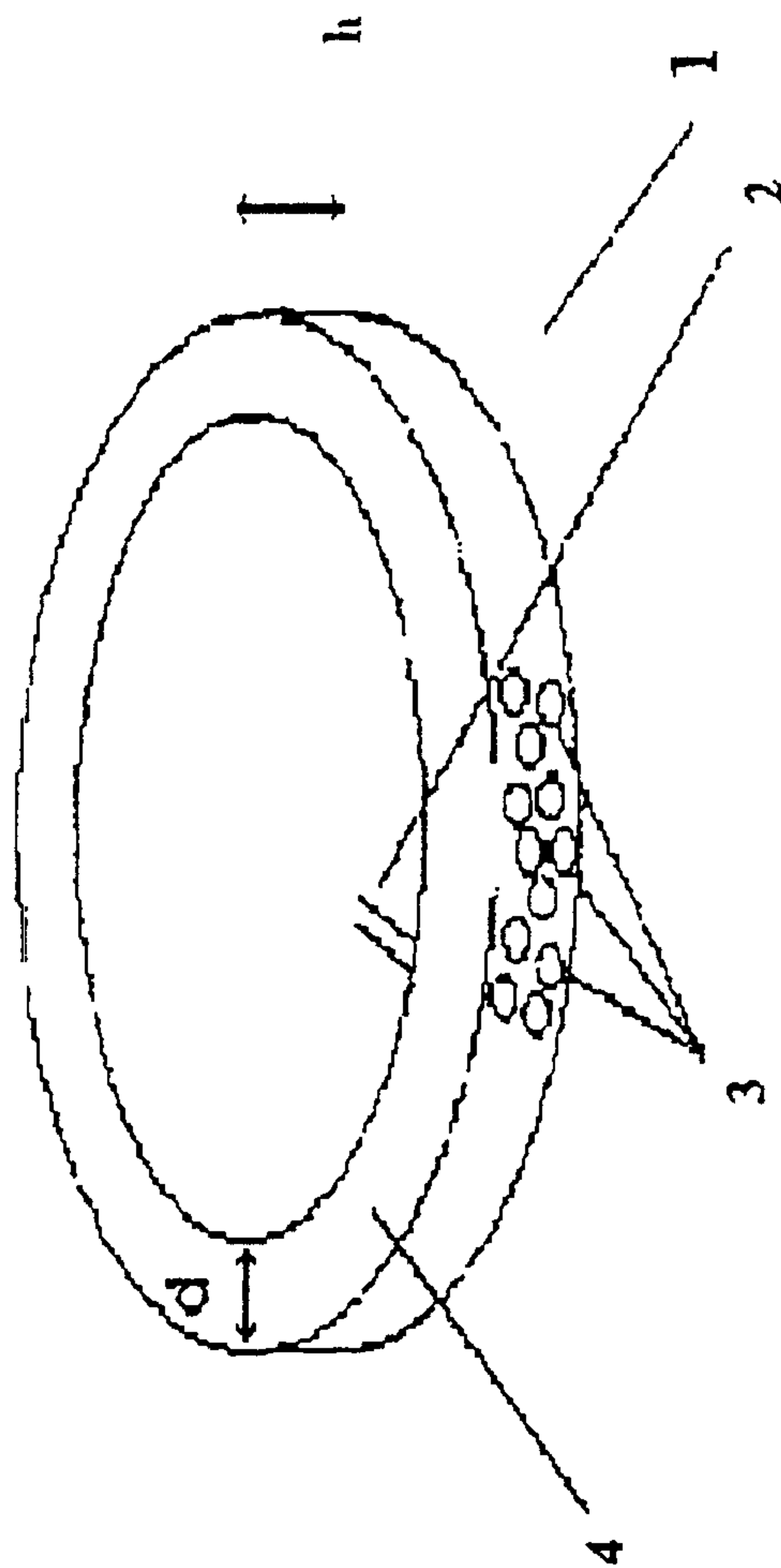


Fig. 2

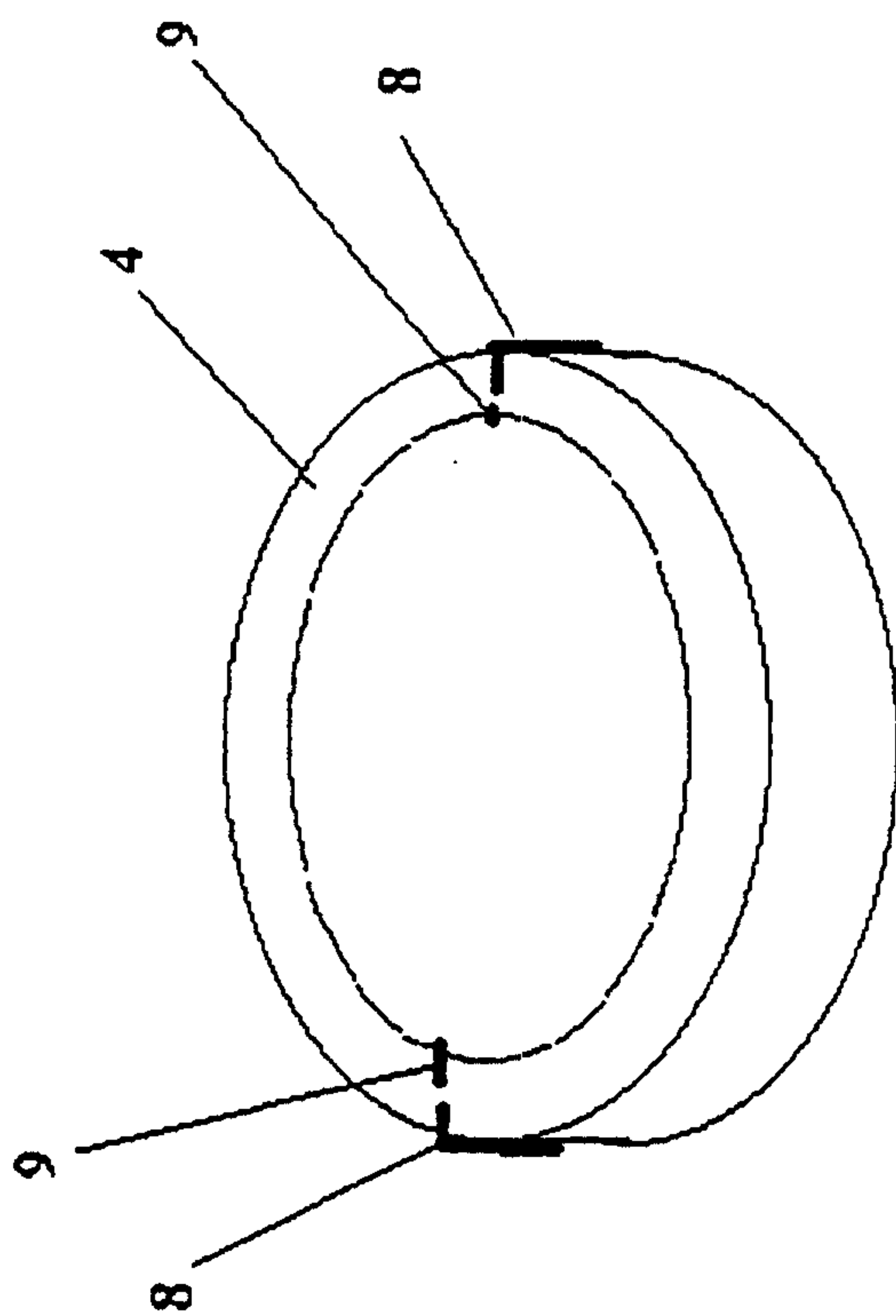


Fig. 3

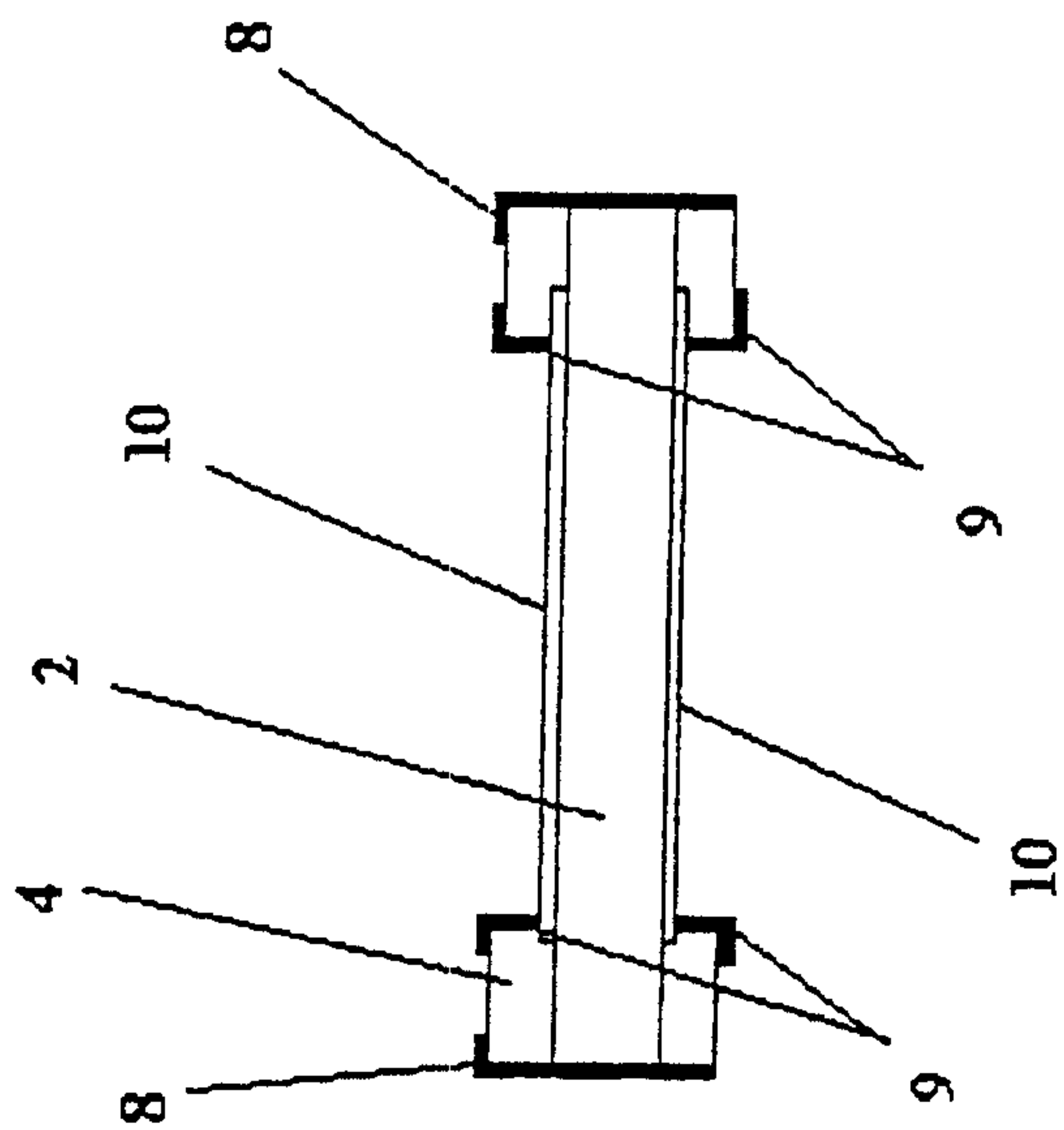


Fig. 3a

