

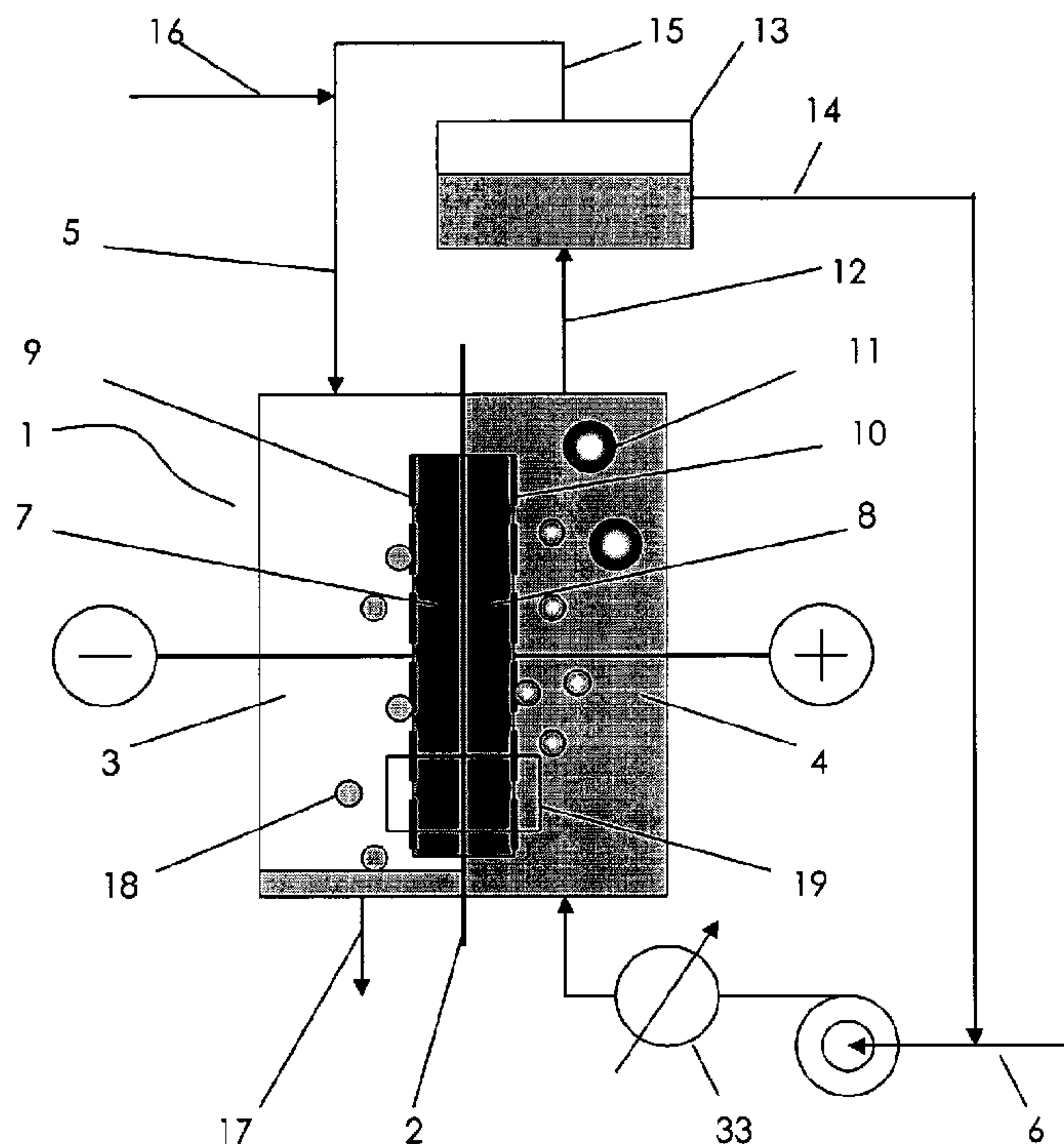


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(54) Title: ELECTROLYSIS CELL FOR HYDROGEN PEROXIDE PRODUCTION AND METHOD OF USE



(57) Abrégé/Abstract:

It is disclosed an electrolysis cell provided with a separator of high hydraulic permeability for the production of diluted hydrogen peroxide with high faradic efficiency. The separator is equipped with an oxygen-fed gas-diffusion cathode and with an anode activated with a catalyst for oxygen evolution. The high faradic efficiency of hydrogen peroxide generation is allowed by the dilution of product hydrogen peroxide by the anolyte crossing the permeable separator, and by keeping the operating temperature at values below 50°C.

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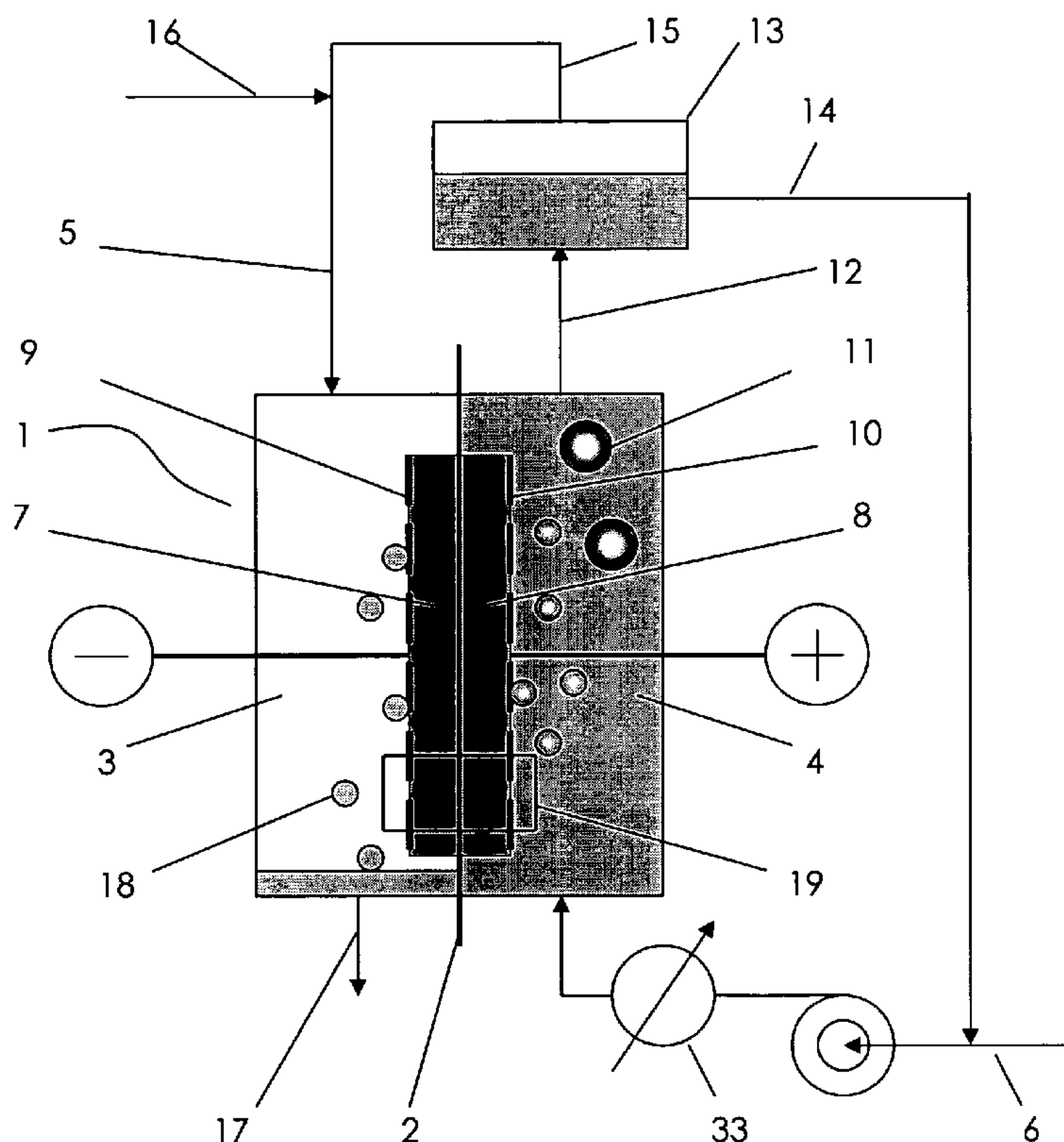
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(54) Title: ELECTROLYSIS CELL FOR HYDROGEN PEROXIDE PRODUCTION AND METHOD OF USE



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ELECTROLYSIS CELL FOR HYDROGEN PEROXIDE PRODUCTION AND METHOD OF USE

Background of the Invention

- 5 Hydrogen peroxide is an oxidant utilised in several applications such as chemical epoxidation processes, waste-water purification, sterilisation of industrial cooling circuits, treatment of electronic integrated circuits, whitening in textile and paper industries. In these applications, hydrogen peroxide is particularly appreciated as it doesn't generate any noxious residues, the only final product consisting of water.
- 10 The manufacturing process currently employed is known as anthraquinone process, wherein ethylanthraquinone (or derivatives thereof) dissolved in a suitable organic solvent is sequentially reduced and oxidised with final generation of a 20% hydrogen peroxide primary solution, subsequently concentrated by distillation. This process is suitable for plants of big capacity, typically 50000 t/yr or more, the final product being distributed to the
- 15 different users in tankers or steel containers as 35-50% hydrogen peroxide solution.

The users must therefore accept all the inconveniences associated with the decay of stored hydrogen peroxide concentration and with the handling of the tanks: to appreciate the importance of the latter item, it will suffice to remind that the sterilisation treatment of an industrial cooling circuit characterised by a 50.000 m³/h flow-rate and

20 by an injection of as little as 2 parts per million hydrogen peroxide requires about 2500 m³/yr of 35% solution.

Some application furthermore require hydrogen peroxide free of noxious (in the case of waste-water purification) or adsorbable (in the case of integrated circuit treatment) organic impurities. Under the latter standpoint, the use of hydrogen peroxide obtained by means of

25 the anthraquinone process is problematic, since the commercial product may contain organic substances up to 100 ppm as well as non-negligible traces of metals, wherein the organic substances and the metal are respectively released by the process solvent and by the plant machinery that may be subject to some corrosion: the known methods for treating hydrogen peroxide concentrated solutions do not seem capable of decreasing the impurities to the

30 levels required by the most critical applications.

It is hence clear that a process suited to the localised production of highly pure hydrogen peroxide would be certainly received with favour by at least part of the users. Processes of this kind are known from the technical literature: both purely chemical processes based on the direct combination of oxygen and

hydrogen on suitable catalysts in the presence of adequate additives at controlled temperature and pressure conditions (see DE 198 17 794 and WO 99/41190) and electrochemical processes were in fact proposed. For instance, electrochemical processes capable of producing dissolved hydrogen peroxide at a concentration of 1-3% in alkaline electrolytes, typically 5-10% sodium hydroxide, are long known, as reported in Chemie Ingenieur Technik 49, 1977 (11), page 911 and in Fifth International Forum on Electrolysis in the Chemical Industry, Electrosynthesis Inc., Fort Lauderdale, Florida (USA), 1991.

This process presents an interesting faradic efficiency (expressed as percentage of electric current effectively used for generating hydrogen peroxide), but is also affected by two important drawbacks, the former being represented by the presence of an alkaline electrolyte which in fact narrows the number of applications of product hydrogen peroxide: for instance, in the industrial cooling plants it is largely preferred the addition of sterilising agents not altering the pH of circulating water, while in the cleaning treatment of integrated circuits the agents employed, which must be easily decomposable without forming secondary products, must not contain additional components except at minimum levels, in the order of magnitude of parts per billion at most.

The latter drawback is given by the criticality of operation of gas-diffusion electrodes used for the conversion of oxygen to hydrogen peroxide, when these necessarily porous electrodes are in contact with a liquid phase, in this case the alkaline solution. Since industrial cells are tall, the consequent hydraulic head determines a flooding of the gas-diffusion electrode in its lower portion, which practically stops functioning properly. For this reason, the design of electrolysis cells equipped with gas-diffusion electrodes entails a limitation in the height and consequently in the active surface, lessening the productive capacity to such an extent that an industrial application proves not viable.

Some attempts directed to overcome this inconvenience are disclosed in the technical literature, but for the time being they have not been developed enough to make them suitable for a commercial use.

One way to radically solve the problem of internal flooding of oxygen-diffusion electrodes was proposed in EP 0 095 997 and US 5,972,196, which describe a cell subdivided by an ionomer membrane into two compartments, cathodic and anodic, respectively fed with oxygen and with water. The ionomer membrane is provided with two electrodes, cathode and anode, in form of catalytic porous films respectively for the reduction of oxygen to hydrogen peroxide on the

cathode side for evolving oxygen from water on the anode side. The oxygen evolution reaction releases protons which migrate in a hydrated form across the ionomer membrane and react with oxygen in the cathode porous film generating hydrogen peroxide. The membrane isolates the cathode porous film from the hydraulic head established by the water present in the anodic compartment: flooding of the porous cathode is hence no more possible, so that the electrolysis cell may be designed of suitable height for industrial applications. The problem with this kind of process is given by the faradic efficiency of hydrogen peroxide production which, according to the aforementioned US 5,972,196, is around 3-3.5%, with final concentrations of 1 to 1.5%. Such a modest result probably derives from the lack of substantial dilution of generated hydrogen peroxide which is conversely a peculiar feature of the alkaline-type process. In fact, in the process of EP 0 095 997 and US 5,972,196 hydrogen peroxide is diluted by the proton hydration water alone, since water diffusion across currently employed ionomer membranes is not significant: in a simplified calculation, assuming a faradic efficiency of 50% and four water molecules constituting the proton hydration shell, a theoretical hydrogen peroxide concentration around 10% is obtained. At this concentration level, hydrogen peroxide is probably affected by a substantial decomposition rate inside the cathode film, certainly accelerated by traces even minimal of some elements, in particular transition elements and compounds thereof.

20 Summary of the Invention

It is an object of the present invention to provide an electrolytic cell for the production of highly pure hydrogen peroxide overcoming the limitations of the prior art.

In particular, it is an object of the present invention to provide an electrolytic cell for the production of hydrogen peroxide with high faradic efficiency.

25 It is a further object of the present invention to provide a method for the production of highly pure hydrogen peroxide with high faradic efficiency.

Under a first aspect the invention relates to an electrolytic cell for the production of hydrogen peroxide subdivided by a separator characterised by high hydraulic permeability into two compartments, cathodic and anodic, the anodic compartment provided with means for feeding an anolyte consisting of

30

deionised water or of an aqueous electrolytic solution, the cathodic compartment comprising means for feeding oxygen and a porous cathode comprising a catalytic material applied to one surface of the separator for reducing oxygen to hydrogen peroxide. By oxygen feed it is intended, herein
5 and in the following, a feed of either pure oxygen or of a gaseous mixture containing oxygen, optionally consisting of air.

The hydraulic permeability of the separator is preferably such that it allows the passage of an anolyte flow, that is water or aqueous electrolytic solution fed to
10 the anodic compartment, at a flow-rate of 10 to 100 l/h.m².

In one preferred embodiment, the separator is a microporous ion-exchange membrane, or a hydrophilic microporous diaphragm with no ionic conductivity.

According to a preferred embodiment of the present invention, the anolyte is an aqueous solution containing at least one acid selected from the group of sulphuric, phosphoric, perchloric and acetic acid; according to an alternative
15 embodiment, the anolyte is an aqueous solution containing at least one basic compound selected from the group consisting of sodium, potassium and lithium hydroxides and potassium carbonate.
20

In one particularly preferred embodiment, the gas-diffusion cathode comprises a porous catalytic film containing micro-regions of hydrophobic nature stably available for oxygen diffusion and hydrophilic micro-regions stably available for
25 the withdrawal of water mixed with the product hydrogen peroxide.

On the surface opposite the one having the gas-diffusion cathode applied thereto, the separator is equipped with an anode optionally in form of gas-diffusion anode comprising a hydrophilic porous film provided with catalytic
30 material for oxygen evolution; in one alternative embodiment, the anodic compartment of the cell contains an anode consisting of a support in form of punched or expanded sheet, provided with a coating comprising a catalytic material for oxygen evolution.

The cathode catalyst for the reduction of oxygen to hydrogen peroxide is preferably selected from the group consisting of gold, palladium and alloys thereof, graphite and macrocyclic metallocomplexes, for instance metalloporphyrins, optionally dispersed on a conductive support; such
35 materials, with particular reference to graphite and to the optional conductive support, must be free of components capable of decomposing hydrogen
40

peroxide, as known in the art.

The anode catalyst for oxygen evolution is preferably selected among the platinum group metals, alloys and oxides thereof.

5 In a preferred embodiment of the invention, the anolyte comprises one or more hydrogen peroxide stabilising agents.

As regards the process conditions, the cell temperature is preferably kept below 50°C, and even more preferably below 30°C, by controlling the anolyte temperature; oxygen evolved in the anodic compartment may be advantageously recycled to the cathodic compartment together with an at least equal amount of oxygen coming from an
10 external source, optionally ambient air. From the cathodic compartment of the cell of the invention it may be thus advantageously obtained a hydrogen peroxide solution of 1 to 5% by weight concentration, with a faradic efficiency not lower than 50%.

Brief Description of the Drawings

15 The invention will be described hereafter making reference to the following figures, provided for the mere sake of illustration:

- Figure 1 is a scheme of a first embodiment of the electrolysis cell of the invention, provided with gas-diffusion cathode and anode applied on the two surfaces of an ion-exchange membrane of high hydraulic permeability.
- Figure 2 is a magnification of a detail of figure 1.
- 20 - Figure 3 is a detail, analogous to that of figure 2, related to a second embodiment of the cell of the invention, wherein the anodic compartment is equipped with an anode consisting of an expanded sheet provided with a catalytic coating for oxygen evolution and the anolyte is an electrolytic solution.
- 25 - Figure 4 is a detail, analogous to that of figure 2, related to a third embodiment of the cell of the invention, wherein the cell is provided with a microporous membrane and with gas-diffusion cathode and anode and the anolyte is deionised water.
- 30 - Figure 5 is a detail, analogous to that of figure 2, related to a fourth embodiment of the cell of the invention, wherein the cell is provided with a microporous membrane and with gas-diffusion cathode and anode and the anolyte is an electrolytic solution.

Detailed Description of the Preferred Embodiments

Figure 1 represents the side-view of a cell 1 subdivided by a separator 2 into two compartments, cathodic 3 and anodic 4, respectively fed with oxygen 5 and an anolyte 6, either consisting of deionised water or of an aqueous solution containing one or more electrolytes. The separator 2 is characterised by a high permeability to water contained in the anolyte present in the anodic compartment 4. In the embodiment of figure 1 the separator 2 is a membrane consisting of an ion-conducting polymer, equipped on the two surfaces facing the cathodic compartment 3 and the anodic compartment 4 respectively with a gas-diffusion cathode 7 comprising a catalytic material for oxygen reduction to hydrogen peroxide and with an anode 8 comprising a catalytic material for the evolution of oxygen from water. Two electric current distributors 9 and 10, for instance in form of punched sheets, expanded sheets or conductive meshes, are connected to the negative and positive poles of a rectifier (not shown) and are kept in intimate contact with the cathode 7 and the anode 8. The ion-conductive membrane is preferably made of a perfluorinated-type polymer material, capable of withstanding the corrosive action of hydrogen peroxide and of radicals generated as intermediate products in the reactions of generation and decomposition thereof: membranes of such kind are for instance commercialised by the DuPont Company, USA under the trade-mark Nafion[®].

The gas-diffusion cathode 7 comprises a porous film characterised by a controlled ratio of hydrophilicity to hydrophobicity, more particularly by a bimodal structure resulting from a multiplicity of homogeneously distributed substantially hydrophilic micro-regions and substantially hydrophobic micro-regions, whose overall volume ratio is preferably of 0.5 to 2, for instance close to 1. By the term micro-region it is herein intended to define elementary volumes which constitute the porous film, having dimensions indicatively ranging from 1 to 100 μm . The micro-regions comprise pores with an average diameter preferably ranging from 0.01 to 1 μm .

The bimodal structure of the cathode porous film may be obtained according to the prior art by suitably adjusting the relative amounts of the constituents, in particular of catalytic material, hydrophilic material and hydrophobic material, the latter two also acting as binders for the whole assembly. Procedures of such kind are for instance disclosed in US 2003/0068544, US 5,998,058 and EP 0 110 491.

Favourite, although not exclusive, hydrophilic and hydrophobic materials

respectively consist of preferably perfluorinated ionomers identical or similar to those used for the manufacturing of ionomer membranes and fluorinated polymers, preferably polytetrafluoroethylene.

5 The catalytic material for the reduction of oxygen to hydrogen peroxide may be selected from the group consisting of gold, palladium and alloys thereof, graphite and macrocyclic metallocomplexes, for instance metalloporphyrins, optionally dispersed on a conductive support, for instance carbon with various
10 degrees of graphitisation. The conductive supports are used in form of micropowders and are characterised by being free of components, in particular transition elements and compounds thereof, capable of decomposing hydrogen peroxide. By the term micropowders it is herein intended powders having average size of about 0.01 to 1 μm .

15 The anode **8** consists in this case of a gas-diffusion anode comprising a porous film having an entirely and substantially hydrophilic structure, applied to the surface of the separator **2** opposite the cathode according to procedures known in the art and based on the use of mixtures of catalytic materials with hydrophilic materials in a suitable ratio. As for the case of the cathodic film, also
20 in this case the hydrophilic material preferably consists of perfluorinated ionomers similar to those used for the manufacturing of ion-exchange membranes. The use of this type of ionomer has the double advantage of allowing to simultaneously achieve a high level of hydrophilicity in the anodic film and an optimum adhesion to the ionomer membrane.

25 The catalytic material of the anodic film may be selected among the platinum group metals, preferably ruthenium, platinum, iridium, alloys thereof and relative oxides. The catalytic material is employed in form of micropowders, as such or deposited on suitable conductive supports, chemically inert in the
30 strongly oxidising conditions typical of oxygen evolution. While active carbons, even at a high degree of graphitisation, would be severely corroded at the indicated process conditions and hence cannot be taken into consideration, conductive oxides such as non-stoichiometric titanium and tantalum oxides and mixed titanium, niobium and tantalum oxides turn out to be appropriate.

35 During the operation of the cell of figure 1, the anodic compartment **4** is fed with deionised water **6** - whose temperature is optionally regulated by heat exchanger **33** - part of which reacts on the catalytic sites of the anodic porous film **8**, giving rise to oxygen evolution **11** and release of protons which migrate
40 across the membrane together with the water of their hydration shell. The

mixture 12 consisting of product oxygen 11 and residual water is sent to the separator 13: the degassed water 14 is recycled to the cell 1 added with a fresh water feed 6, while separated oxygen 15 is fed to the cathodic compartment 3 together with an equal amount of oxygen coming from an external source 16, for instance air conveyed by a fan or compressor or an oxygen-containing flow produced by an air-enrichment device (not shown in figure 1). Oxygen flowing in the cathodic compartment 3 diffuses across the porosity of the hydrophobic micro-regions of cathode film 7 and, in combination with the protons migrating across the membrane, is reduced to hydrogen peroxide on the active sites of catalytic micropowders. Hydrogen peroxide thus produced, diluted by water transported by protons as a hydration shell and more importantly by water diffusing across the membrane, is withdrawn from the bottom part 17 of the cell cathodic compartment. The hydrogen peroxide dilution with diffused water represents a fundamental feature of the present invention. In fact, if hydrogen peroxide were only diluted by the water transported by protons, as occurs in the processes known in the art, its concentration would be indicatively 10-15%, at which level the decomposition rate inside the cathode film, catalysed by the unavoidable traces of certain impurities, would be certainly high with a consequent sudden decay of the effective faradic efficiency, as known in the art. In the presence of the dilution effect induced by water diffusion across the membrane, the initial concentration of hydrogen peroxide can be remarkably lower than the above indicated value. In particular, it was found that such concentration may be reduced below 5%, preferably within the range 1-3% with a faradic efficiency equal to or higher than 50%.

In order to achieve the above indicated concentrations, with the cell operated at a current density preferably of 1-2 kA/m², the tests carried out demonstrated that the ionomer membrane in accordance with the invention should have a water permeability of 5 to 100 l/h.m², preferably 10 to 50 l/h.m². Such values of permeability can be achieved for instance with perfluorinated ionomer membranes having an equivalent weight below 900, more preferably below 700, and preferably a high cross-linking degree directed to ensure their stability in the presence of water or aqueous solutions. Some methods for the production of this type of membranes are known in the art, for instance according to the disclosure of EP 1 238 999. A similar membrane, preferably 30 to 200 µm thick, may be advantageously provided with an internal reinforcement directed to increase its mechanical resistance - particularly in the presence of pressure differentials across its two faces - and to improve its handling and in general all the operations associated with its installation in the cell. The reinforcement is selected from the group of fibres dispersed in the

polymer bulk, micro-cloths, (for instance expanded micro-cloths), and cloths inserted within the thickness of the membrane.

It was also found that the desired permeability values are also obtained with the optional co-operation of a pressure differential across the first and the second surface of the membrane, wherein such differential is at least 0.1 bar and preferably of 0.3 to 1 bar (pressure in the anodic compartment 4 higher than the pressure in the cathodic compartment 3).

Water diffusion from the anodic compartment 4 to the cathodic compartment 3 is affected, besides the ionomer membrane's own permeability, also by the characteristics of hydrophilicity and hydrophobicity of the cathode 7 and anode 8 porous films. In particular it was observed that the highest water diffusion rates are achieved when the anode porous film 8 is substantially hydrophilic across the whole structure. On the contrary it was verified that such structure is unfit for the cathode porous film 7 since it would lead to a massive internal flooding preventing the diffusion of oxygen to the catalyst active sites, which would hamper the cell operation. On the other hand it was also found that a completely hydrophobic structure hinders water diffusion from the membrane to a substantial extent. To avoid these inconveniences, the structure of porous film 7 must simultaneously comprise, as indicated above, distributed hydrophobic micro-regions homogeneously arranged side-by-side to the corresponding hydrophilic micro-regions. This bimodal structure of the cathode porous film is essential to ensure stable functioning conditions wherein hydrophilic porous regions allow the mixture 18 formed by water coming from separator 2 and hydrogen peroxide produced on the catalytic active sites to be easily discharged from the surface of the cathode film facing the surface in contact with separator 2, while hydrophobic regions free of liquid water permit the quick diffusion of oxygen to the catalytic material active sites. In particular it could be verified that the optimum functioning conditions are achieved when the volumetric ratio of hydrophilic to hydrophobic regions is approximately 1.

This microstructure is sketched in figure 2, which represents the magnification of detail 19 of figure 1, wherein 20 identifies the catalytic micropowder for reducing oxygen to hydrogen peroxide, marked with hexagons for an easier understanding, 21 the micropowder of hydrophobic nature (squares), preferably polytetrafluoroethylene, distributed so as to create hydrophobic micro-regions 22, 23 the micropowder of hydrophilic nature (circles), preferably an ionomer identical or similar to the one used for the manufacturing of the membrane, preferably a perfluorinated ionomer, substantially localised in the hydrophilic

regions 24, 25 the catalytic micropowder for oxygen evolution from water (hexagons),
26 the hydrophilic micropowder (circles), again preferably an ionomer identical or
similar to the one used for the manufacturing of the membrane, preferably a
perfluorinated ionomer, homogeneously distributed to make the whole anode porous
5 film hydrophilic, the oxygen bubbles evolved from the anode porous film. The porosity
both of the hydrophilic and hydrophobic micro-regions of the cathode film, and of the
whole anode film, consists of the three-dimensional network of the interspaces
between the various micropowders. The components of figure 2 in common with those
of figure 1 are identified by the same reference numerals, while the migration of the
10 hydrated protons and the flow of water across the membrane and the oxygen diffusion
across the cathode porous film are respectively indicated by arrows 27, 28, and 29.

The above illustrated process may be modified by replacing the deionised water feed
with an aqueous solution feed containing one or more electrolytes, preferably selected
from the group of sulphuric, phosphoric, perchloric and acetic acid, optionally added
15 with additional electrolytes, such as for instance sodium or potassium salts of the same
acids.

Aqueous solutions containing acids and optionally salts thereof are characterised by a
substantial electrical conductivity, therefore this kind of feed allows resorting to an
alternative design of anode consisting of punched sheets, expanded sheets or meshes
20 placed in contact with the second surface of the membrane or at a certain distance
therefrom, preferably not exceeding 3 mm. The testing has demonstrated that a similar
constructive solution presents higher operating voltages, but also that it is
characterised by a higher simplicity and by reduced manufacturing costs. The
construction material of sheets and meshes, having to be electrically conductive and
25 resistant to the aggressiveness of the aqueous solutions fed to the anodic
compartment, is preferably a metal selected from the group consisting of titanium,
zirconium, niobium, tantalum, alloys thereof and nickel alloys of high chromium content.
Sheets and meshes are further provided with a catalytic coating for the evolution of
oxygen from water in acidic environment as known in the art, consisting of platinum
30 group metals, alloys and oxides thereof, preferably iridium oxide or iridium and
ruthenium mixed oxide optionally added with titanium, tantalum or niobium oxide.

This second cell embodiment is shown in figure 3 which represents a modification
of the detail illustrated in figure 2: the components in common with

those of figure 2 are identified by the same reference numerals while **30** indicates a sketch of the side-view of an expanded sheet in a parallel position to the membrane at a distance **31**.

5 It was verified that the optional presence of a microporosity in the ionomer membrane of the cell of figures 1, 2 and 3 does not raise any particular concern associated with its functioning, since the only gas present in the two compartments cathodic and anodic is oxygen, the typical hydrophilicity of the ionomer material favouring moreover the penetration of water or aqueous
10 solution contained in the anodic compartment in the micropores, with a substantial sealing effect: this feature facilitates remarkably the manufacturing of the required ionomer membranes even at a very reduced thickness, differently to what happens for example with ionomer membranes for fuel cells, wherein the gases in the cathodic and anodic compartment are oxygen and
15 hydrogen and wherein liquid water is not always present.

Conversely it was found that for the process of the invention, microporosity may prove an important property of the membrane allowing to obtain more easily water diffusion flows up to 100 l/h.m² with modest pressure differentials, even
20 lower than 0.1 bar, as required in order to obtain dilute and stable hydrogen peroxide solutions. Microporous membranes of this kind are disclosed in EP 1 238 999. Microporosity can also be obtained by embedding suitable fillers in the ionomer membranes in form of microporous particles of hydrophilic materials, such as for instance several types of oxides, for example silica,
25 alumina, titanium dioxide and the like, as widely known from the technical literature which also discloses several methods of production.

Figure 4 represents the detail, analogous to that illustrated in figure 2, related to a third embodiment of cell fed with deionised water with a modification of the
30 microporous nature of the ionomer membrane, wherein **32** identifies the micropores, the common elements with figure 2 being indicated by the same numerals. In the present context, micropores indicates the pores crossing the whole thickness of the membrane preferably characterised by average diameters of 0.01 to 1 µm. This kind of microporosity proves necessary to avoid
35 that the effect of pressure existing in the anodic compartment determines some sort of flooding of the cathode porous film, detrimental for the regular functioning.

In figure 4 there is evidenced the localisation of water diffusion and proton
40 migration in distinct areas: in particular, the water flow **28** is essentially

localised within the microporosity, while conversely, due to the poor electrical conductivity of deionised water, hydrated proton migration **27** is necessarily limited to the bulk of the ionomer membrane.

5 When the anodic compartment is fed with aqueous solutions containing electrolytes, for instance selected from the group of sulphuric, phosphoric, perchloric and acetic acid, optionally containing the sodium and potassium corresponding salts, at a concentration indicatively equal to or higher than 0.1 M, and thus characterised by a substantial electrical conductivity, also proton
10 migration **27** turns out to be localised within the micropores, as sketched in figure 5. In this situation it was verified that the separator may advantageously consist of a microporous diaphragm, made of a chemically stable material in the operating conditions but lacking any ionic conductivity, selected from the group of polysulphones, polyetherketones, polyetheretherketones,
15 polybenzimidazoles and other chemically stable polymers, provided they are made hydrophilic, for instance by suitable additives.

Feeding the anodic compartment with an aqueous solution allows making use also with cells equipped with a microporous separator (ionomer membrane or
20 diaphragm) of the above seen anode design represented by punched sheets, expanded sheets or meshes put in contact with the second surface of the membrane or spaced therefrom, preferably with a gap not higher than 3 mm.

It is apparent that the aqueous solution flow across the microporosity of the separator (membrane or diaphragm) implies that the product hydrogen
25 peroxide also contains the same electrolyte present in the aqueous solution. Such presence is acceptable for applications in the field of cooling circuit sterilisation or waste-water treatment, while being certainly not compatible with superficial cleaning treatments of electronic integrated circuits: in the latter case
30 the cell anodic compartment must be compulsorily fed with totally deionised water, and it is therefore necessary to make use of different embodiments of the present invention.

It was found that satisfactory results in terms of final hydrogen peroxide
35 concentration and faradic efficiency are also obtainable when the aqueous solution fed to the anodic compartment of the cell is of the alkaline type, preferably containing sodium, potassium or lithium hydroxide or potassium carbonate.

40 The water or aqueous solution fed to the cell anodic compartment may be

added with hydrogen peroxide-stabilising agents, provided the latter are compatible with the subsequent application, in order to further minimise the decomposition rate of the dilute product solution: some stabilising agents, as indicated in Encyclopaedia of Chemical Technology, Kirk - Othmer, Vol. 11, consist for example of sodium pyrophosphate, colloidal tin oxide, alkaline silicates and chelating compounds such as hydroxyquinoline and salts of ethylenediaminetetraacetic acid.

It was finally found that an additional stabilisation of hydrogen peroxide solutions produced by the method of the present invention is obtainable by controlling the operating temperature typically below 50°C, preferably below 30°C, for instance by means of heat exchanger 33 (figure 1) inserted on the feed-stream of cell 1.

The previous description is not intended to limit the invention, which may be used according to different embodiments. The scope of the claims should not be limited by the preferred embodiments set forth in the examples, but should be given the broadest interpretation consistent with the description as a whole.

Throughout the description and claims of the present application, the term "comprise" and variations thereof such as "comprising" and "comprises" are not intended to exclude the presence of other elements or additives.

CLAIMS:

1. Electrolysis cell for hydrogen peroxide production comprising a membrane subdividing the cell into a cathodic compartment and an anodic compartment, said membrane being an ionomer membrane having an equivalent weight below 700 and being provided with a first surface facing the cathodic compartment having a gas-diffusion cathode applied thereto comprising a catalytic porous film for the reduction of oxygen to hydrogen peroxide wherein said catalytic porous film of said gas-diffusion cathode comprises at least one hydrophobic material, at least one hydrophilic material and at least one catalytic material for reducing oxygen to hydrogen peroxide and has a bimodal internal structure comprising hydrophobic micro-regions and hydrophilic micro-regions, and with a second surface facing the anodic compartment, said cathodic compartment comprising means for feeding oxygen, said anodic compartment comprising means for feeding an aqueous anolyte and an anode equipped with a catalyst for oxygen evolution.
2. The cell of claim 1 wherein said hydrophobic and hydrophilic micro-regions comprise pores with an average diameter of 0.01 to 1 μm .
3. The cell of claim 1 or 2 wherein said hydrophobic and hydrophilic micro-regions have average dimensions of 1 to 100 μm .
4. The cell of any one of claims 1 to 3 wherein the volumetric ratio of said hydrophobic micro-regions to said hydrophilic micro-regions is 0.5 to 2.
5. The cell of any one of claims 1 to 4 wherein said hydrophilic material is an ion-conductive perfluorinated polymer.
6. The cell of any one of claims 1 to 5 wherein said catalytic material is selected from the group consisting of gold, palladium and alloys thereof, graphite and macrocyclic metallocomplexes.

7. The cell of claim 6 wherein said catalytic material is dispersed on a conductive support free of components capable of decomposing hydrogen peroxide.
8. The cell of any one of claims 1 to 7 wherein said anode is a gas-diffusion anode comprising a hydrophilic porous film applied to said second surface of said membrane equipped with a catalyst for oxygen evolution.
9. The cell of any one of claims 1 to 7 wherein said anode comprises a support in form of conductive punched sheet, expanded sheet or mesh equipped with a catalytic coating for oxygen evolution.
10. The cell of any one of claims 1 to 9 wherein said anodic catalyst for oxygen evolution is selected from the group of platinum group metals, alloys and oxides thereof.
11. A process for the production of an aqueous solution of hydrogen peroxide of 1 to 5% by weight concentration comprising the simultaneous or sequential steps of providing an electrolysis cell which comprises a membrane subdividing the cell into a cathodic compartment and an anodic compartment, said membrane having an equivalent weight below 700 and being provided with a first surface facing the cathodic compartment having a gas-diffusion cathode applied thereto comprising a catalytic porous film for the reduction of oxygen to hydrogen peroxide wherein said catalytic porous film of said gas-diffusion cathode comprises at least one hydrophobic material, at least one hydrophilic material and at least one catalytic material for reducing oxygen to hydrogen peroxide and has a bimodal internal structure comprising hydrophobic micro-regions and hydrophilic micro-regions and with a second surface facing the anodic compartment, said cathodic compartment comprising means for feeding oxygen, said anodic compartment comprising means for feeding an aqueous anolyte and an anode equipped with a catalyst for oxygen evolution, feeding oxygen to the cathodic compartment, feeding an aqueous anolyte to the anodic compartment, and applying an electric current to said cell while establishing an anolyte flow-rate of 10 to 100 l/h.m² across said separator.

12. The process of claim 11 wherein said cell is the cell of any one of claims 1 to 10.
13. The process of claim 11 or 12 wherein said aqueous anolyte consists of deionised water.
14. The process of claim 11 or 12 wherein said aqueous anolyte contains at least one electrolyte.
15. The process of claim 14 wherein said at least one electrolyte is selected from the group consisting of sulphuric, phosphoric, perchloric and acetic acid, their sodium and potassium salts, sodium, potassium and lithium hydroxides and potassium carbonate.
16. The process of any one of claims 11 to 15 further comprising setting the temperature of said anolyte feed at a value not higher than 50°C.
17. The process of claim 16 wherein said temperature set of said anolyte feed is carried out by means of a heat exchanger.
18. The process of any one of claims 11 to 17 wherein said anolyte is added with at least one hydrogen peroxide stabilising agent.
19. The process of claim 18 wherein said at least one hydrogen peroxide stabilising agent is selected from the group consisting of sodium pyrophosphate, colloidal tin oxide, alkaline silicates, chelating compounds and salts of ethylenediaminetetraacetic acid.
20. The process of any one of claims 11 to 18 wherein said oxygen feed to the cathodic compartment comprises a recycle of oxygen generated on said anode of said anodic compartment mixed with an at least equal amount of oxygen coming from an external source.
21. The process of claim 20 wherein said external source is ambient air.

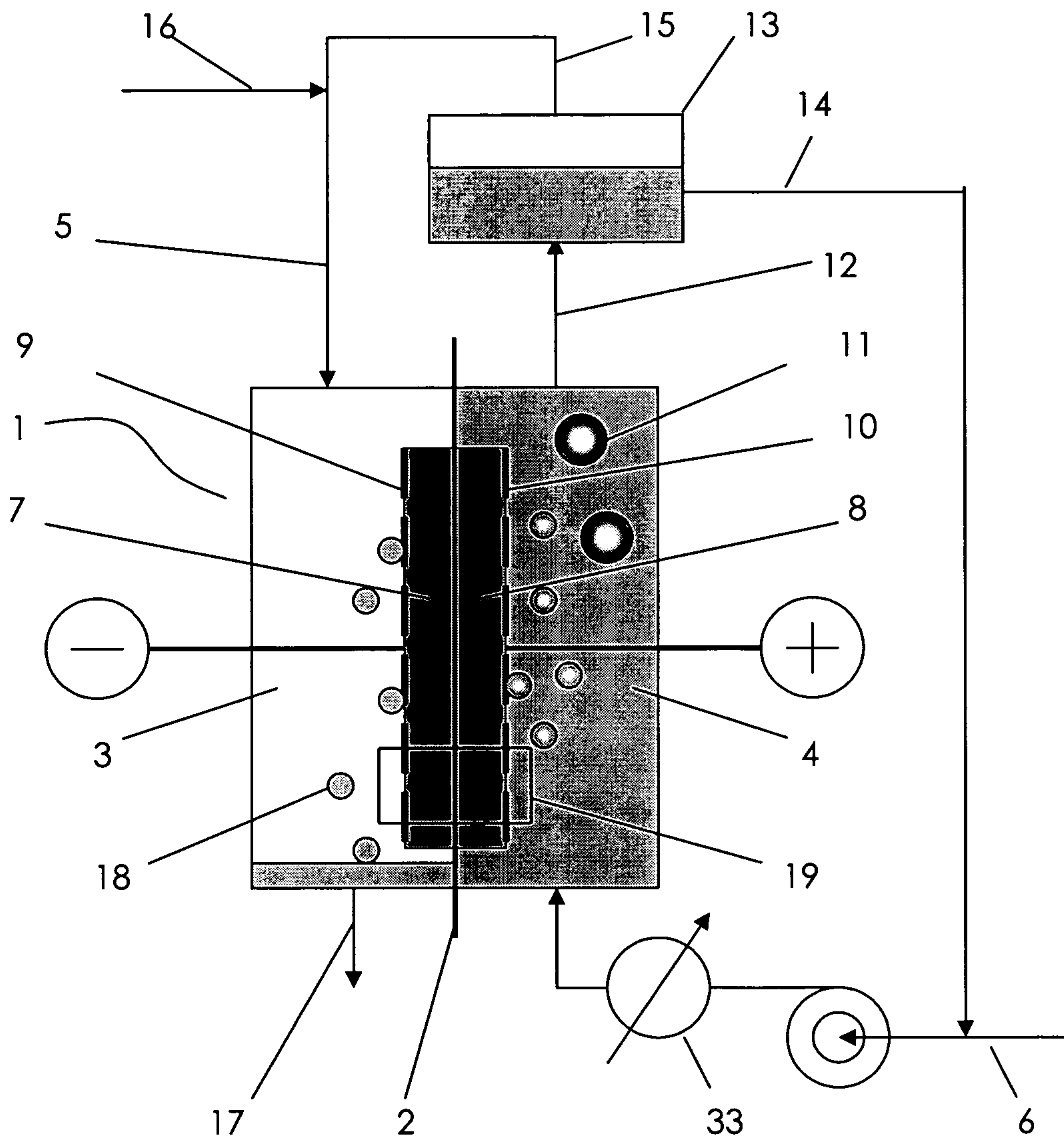


Fig. 1

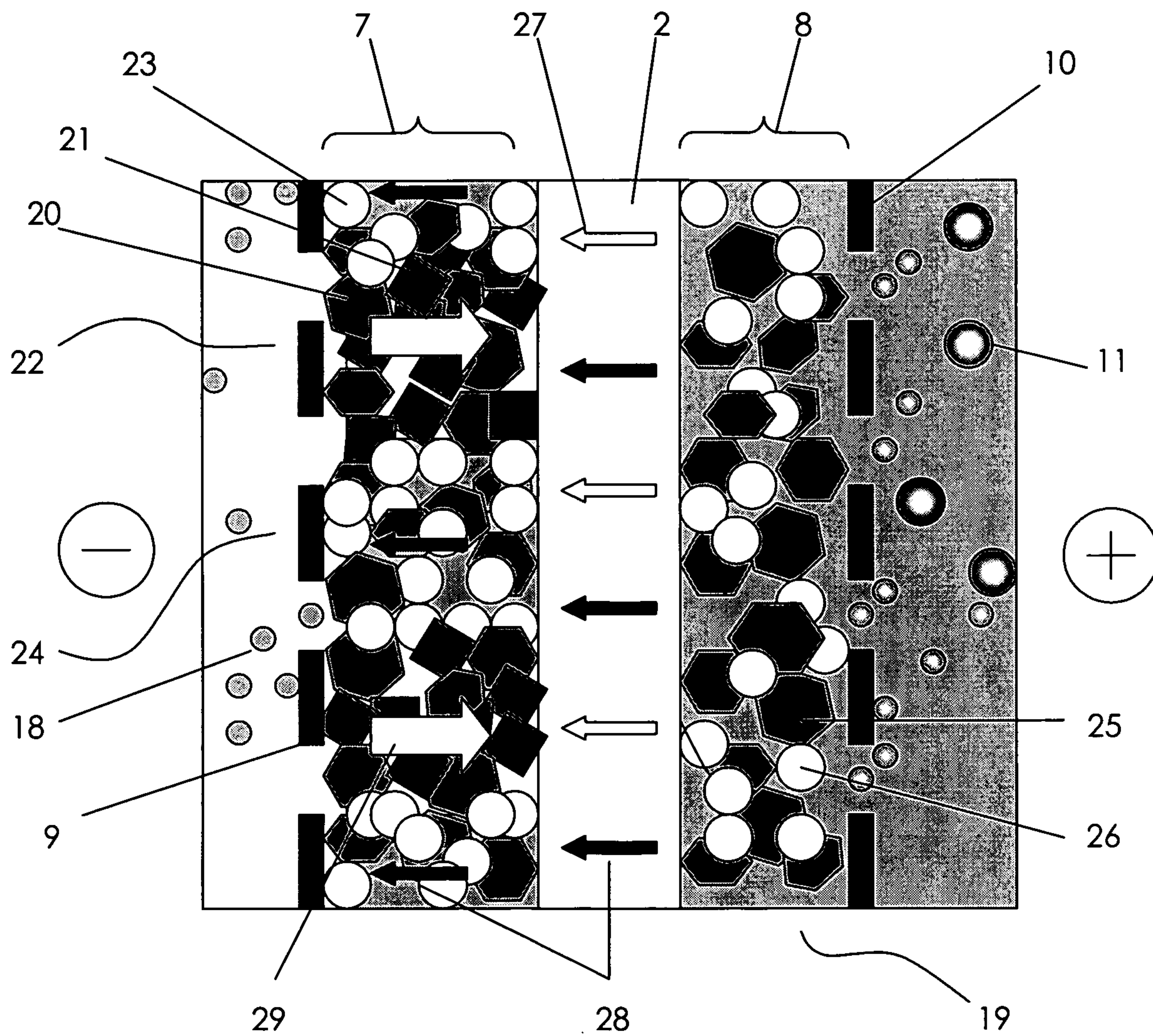


Fig. 2

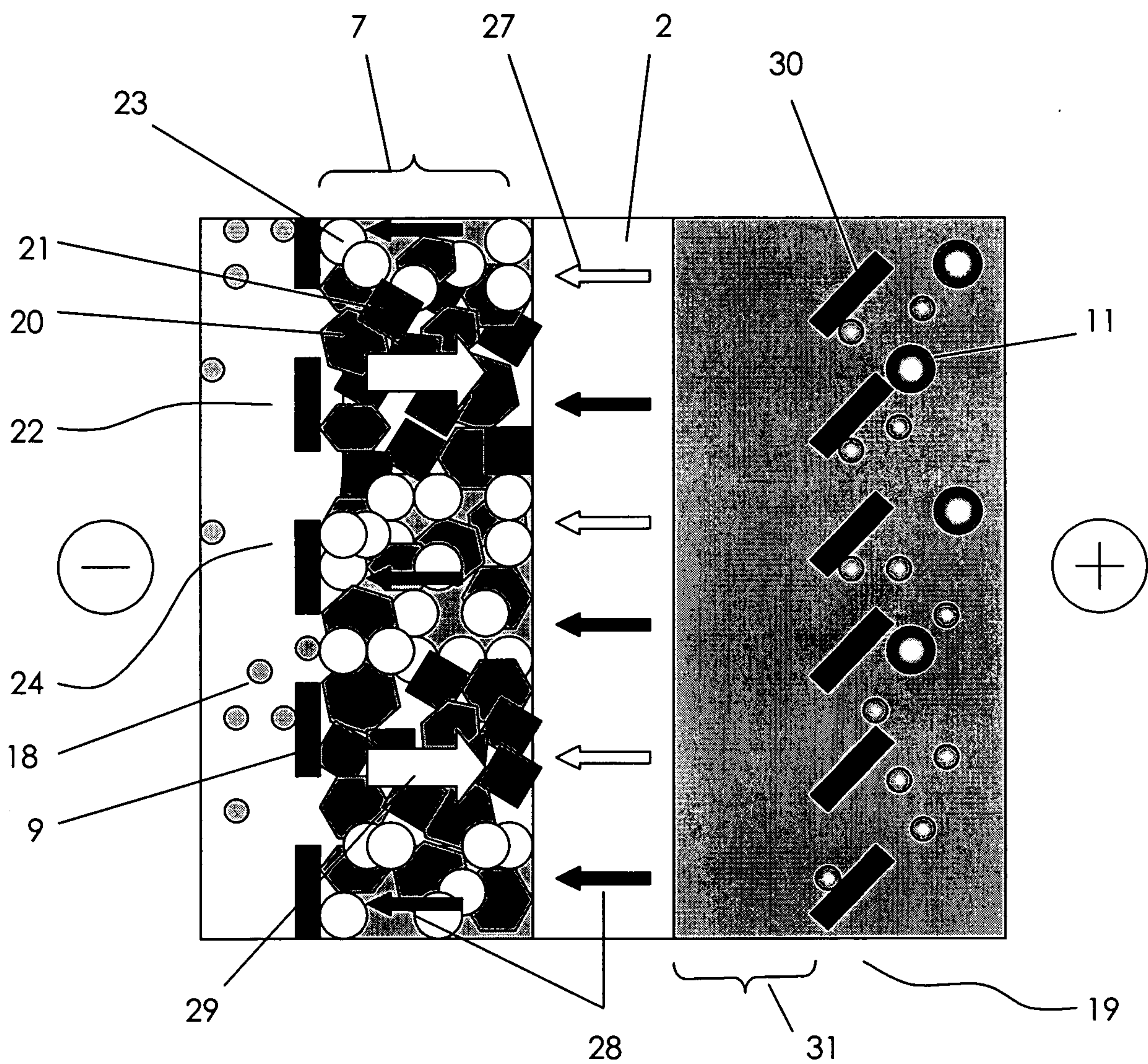


Fig. 3

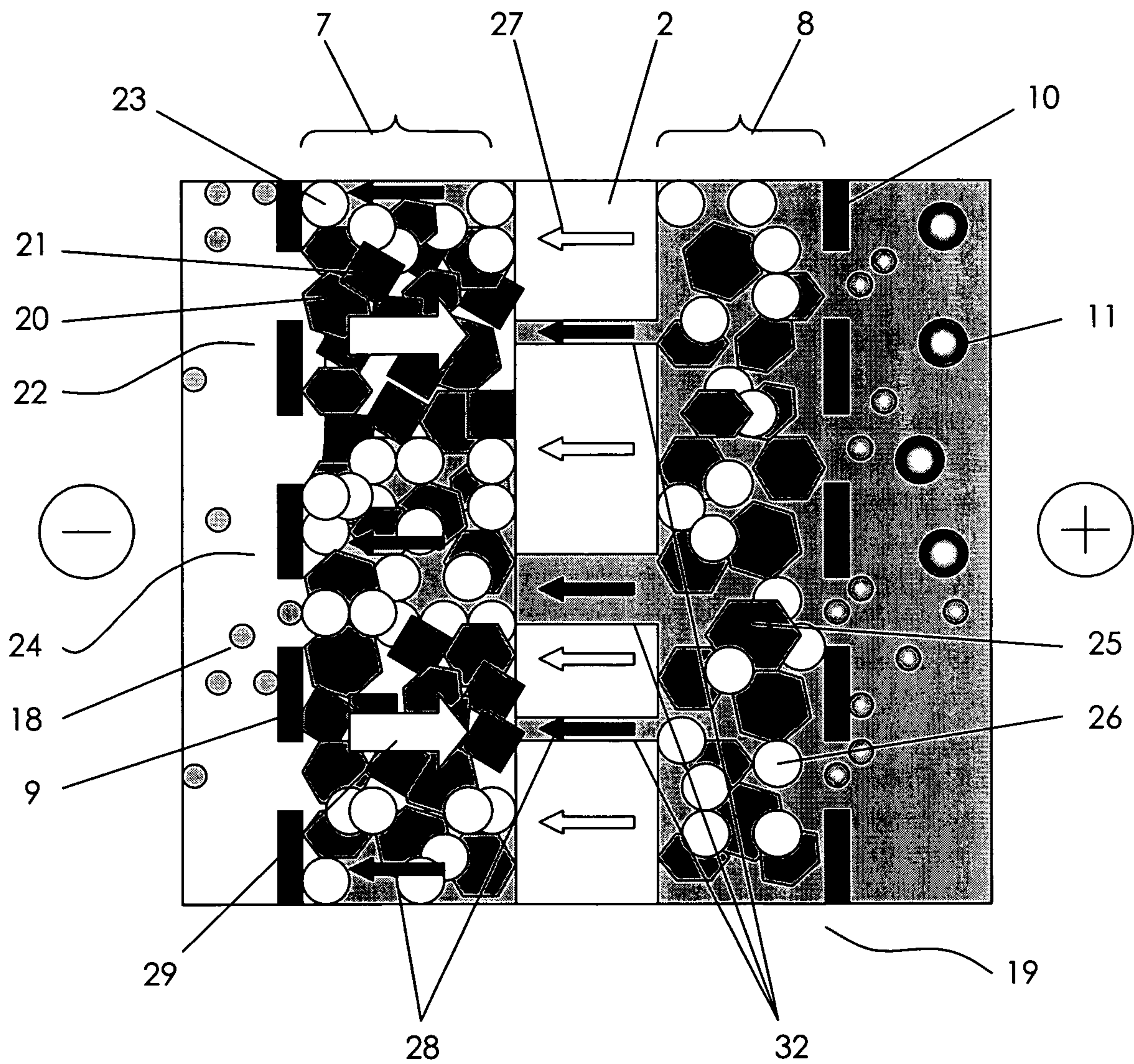


Fig. 4

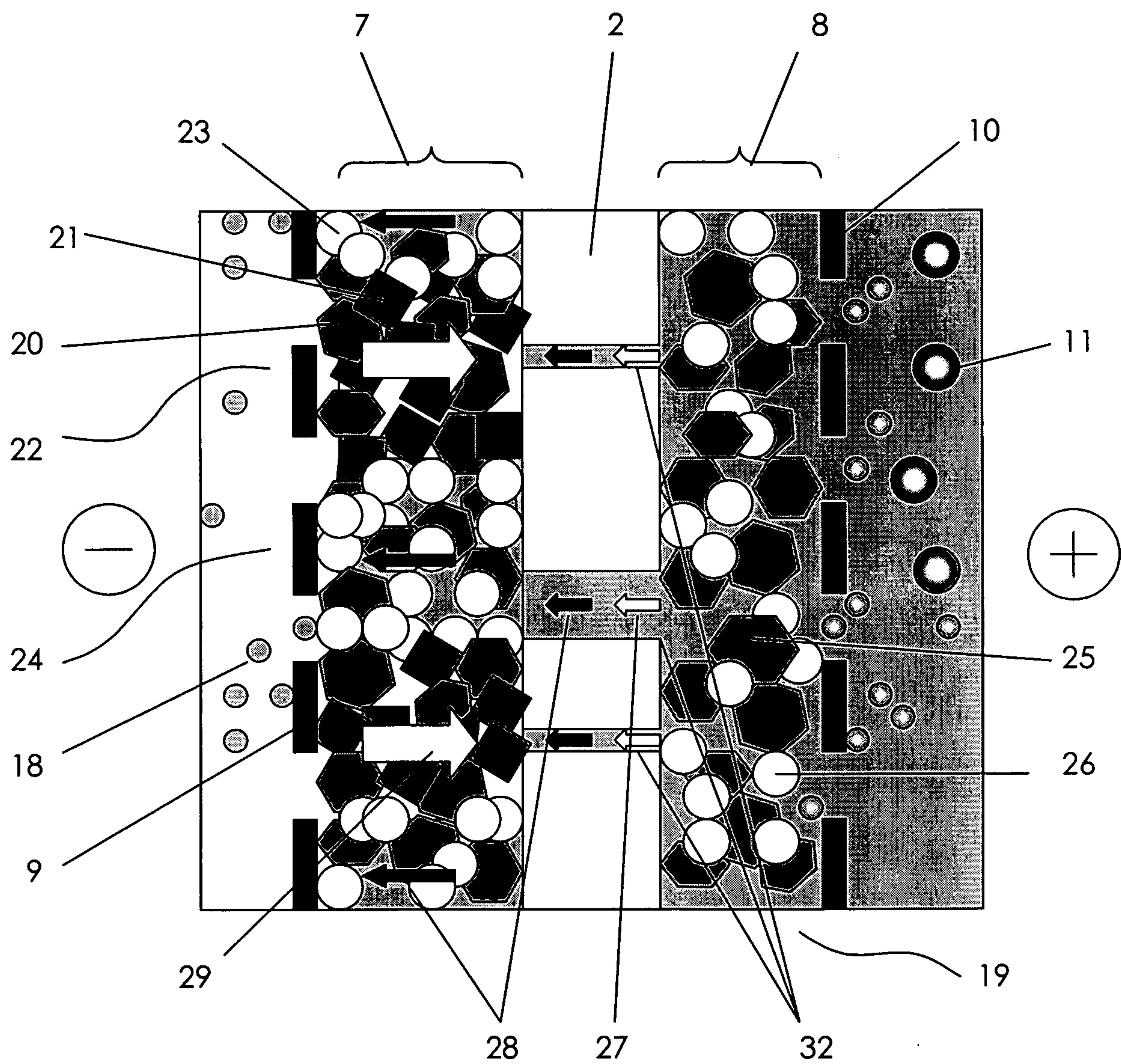


Fig. 5

