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(54) ELECTROCHEMICAL REACTING ELECTRODE, METHOD OF MAKING, AND APPLICATION DEVICE

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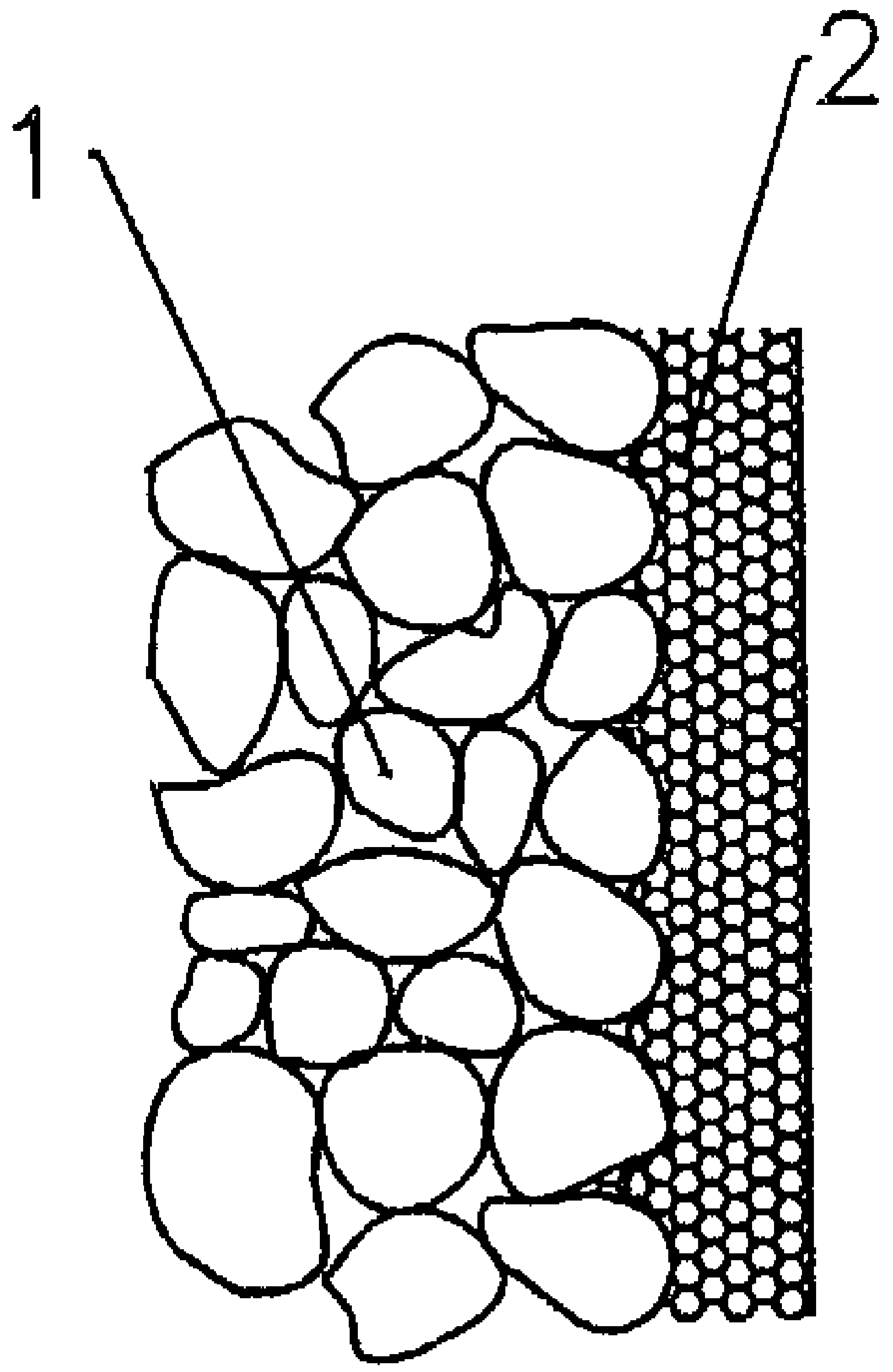
(57) ABSTRACT

The present invention refers to methods for the manufacture of gas-diffusion electrodes to be used for water electrolysis and ozone production, as well as electrodes for fuel cells and other electrochemical devices. A portion of protons of an ion-exchange polymer is substituted in the channels of a channel-cluster structure of an ion-exchange polymer with cations of metal catalyst. This substitution is performed via the ion exchange process. Then said cations are electrochemically reduced in the form of metal particles of a catalyst on those areas of substrate where the latter is in contact with the channels of the channel-cluster structure of the ion-exchange polymer layer.



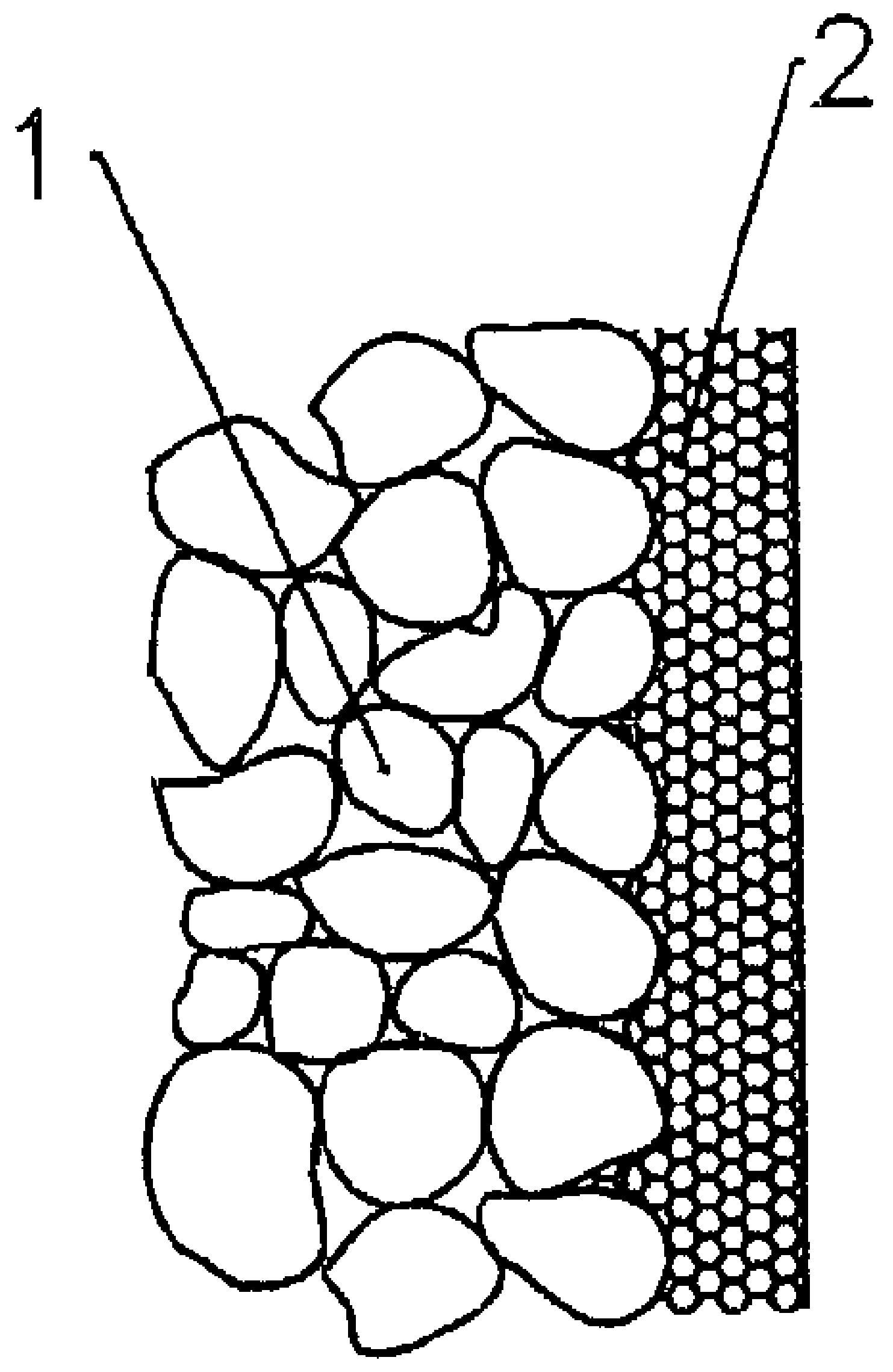


Fig. 1

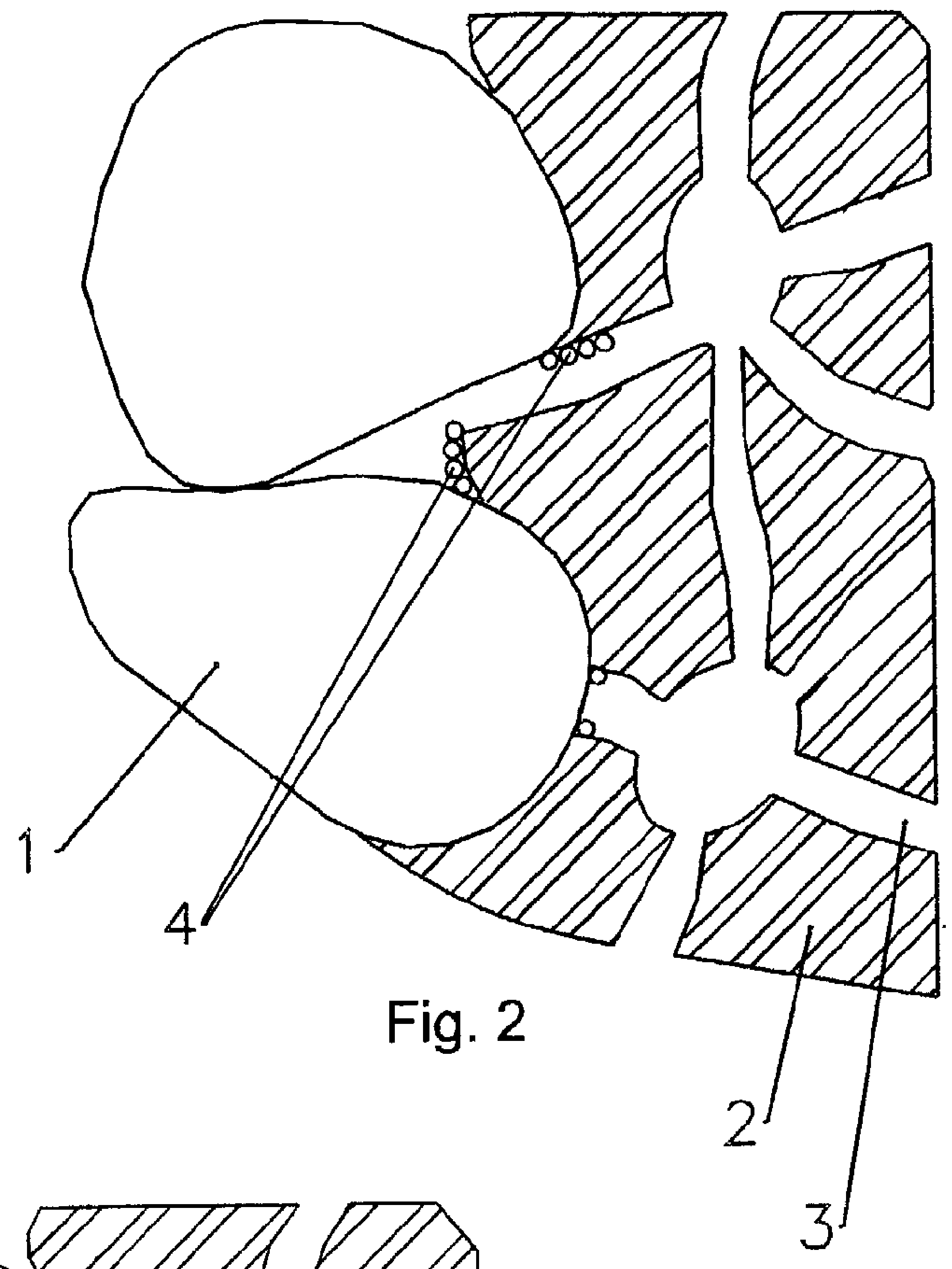


Fig. 2

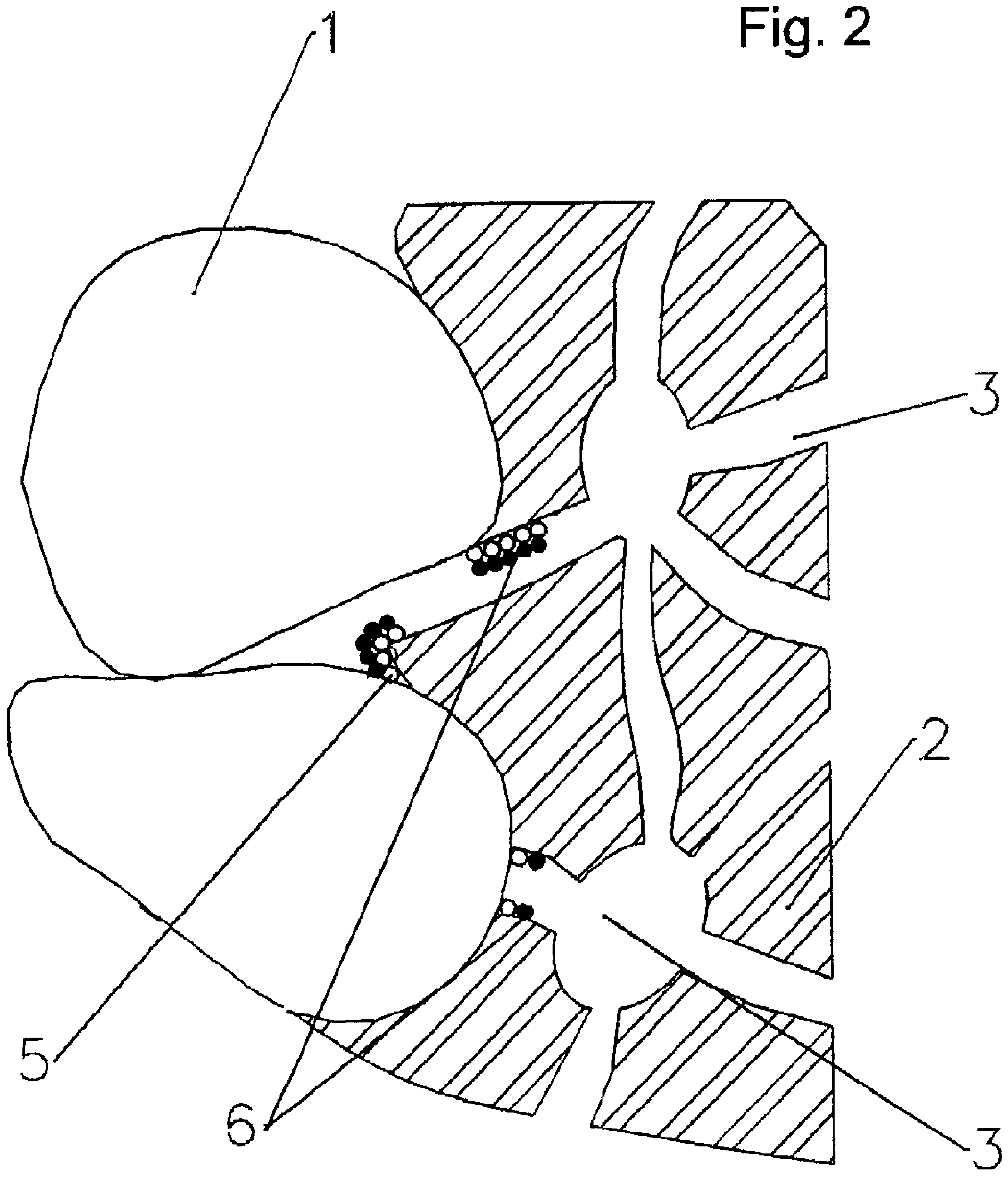
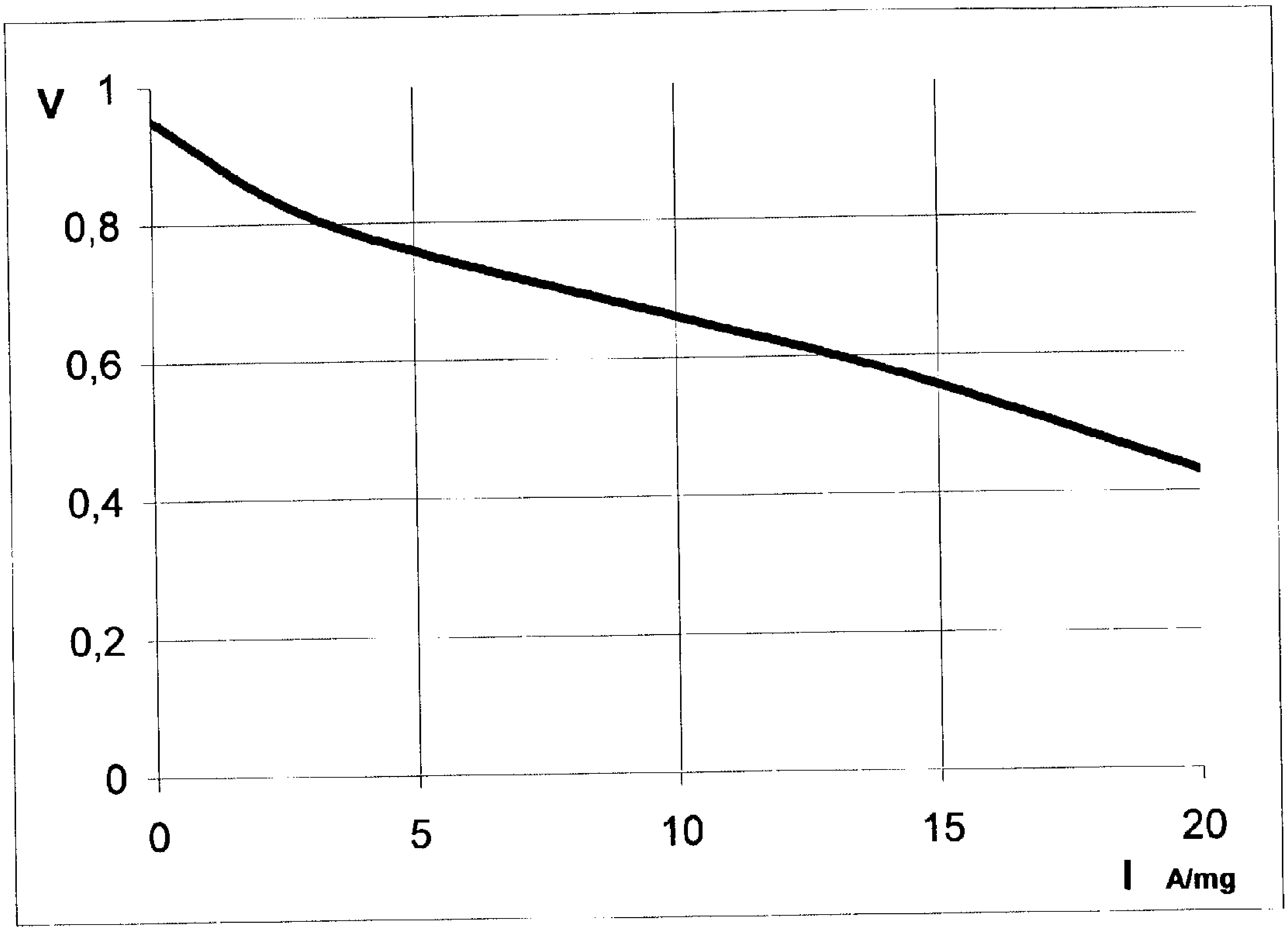


Fig. 3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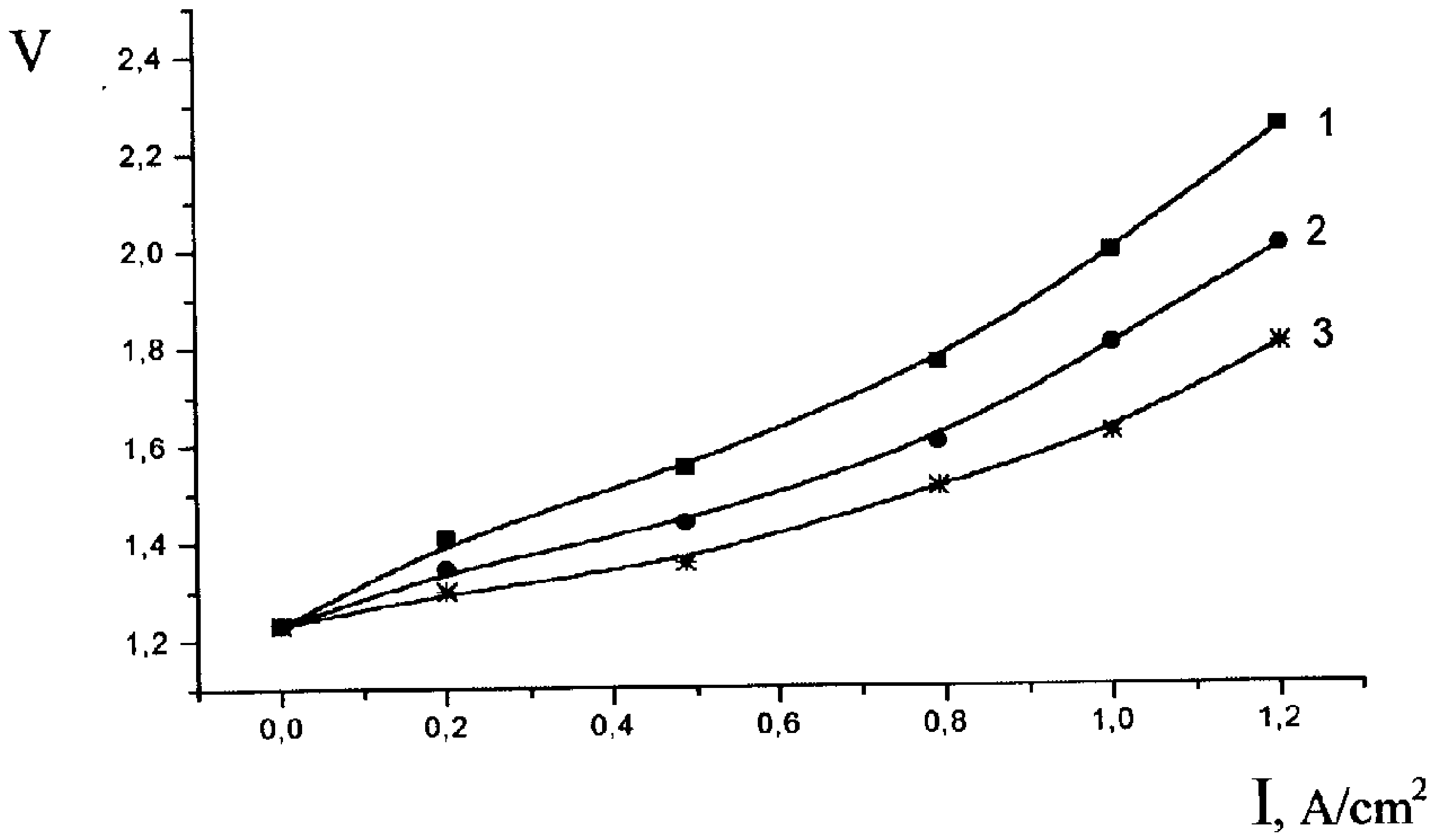
I A/mg

Fig. 4


V
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I, A/cm²
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Fig. 5

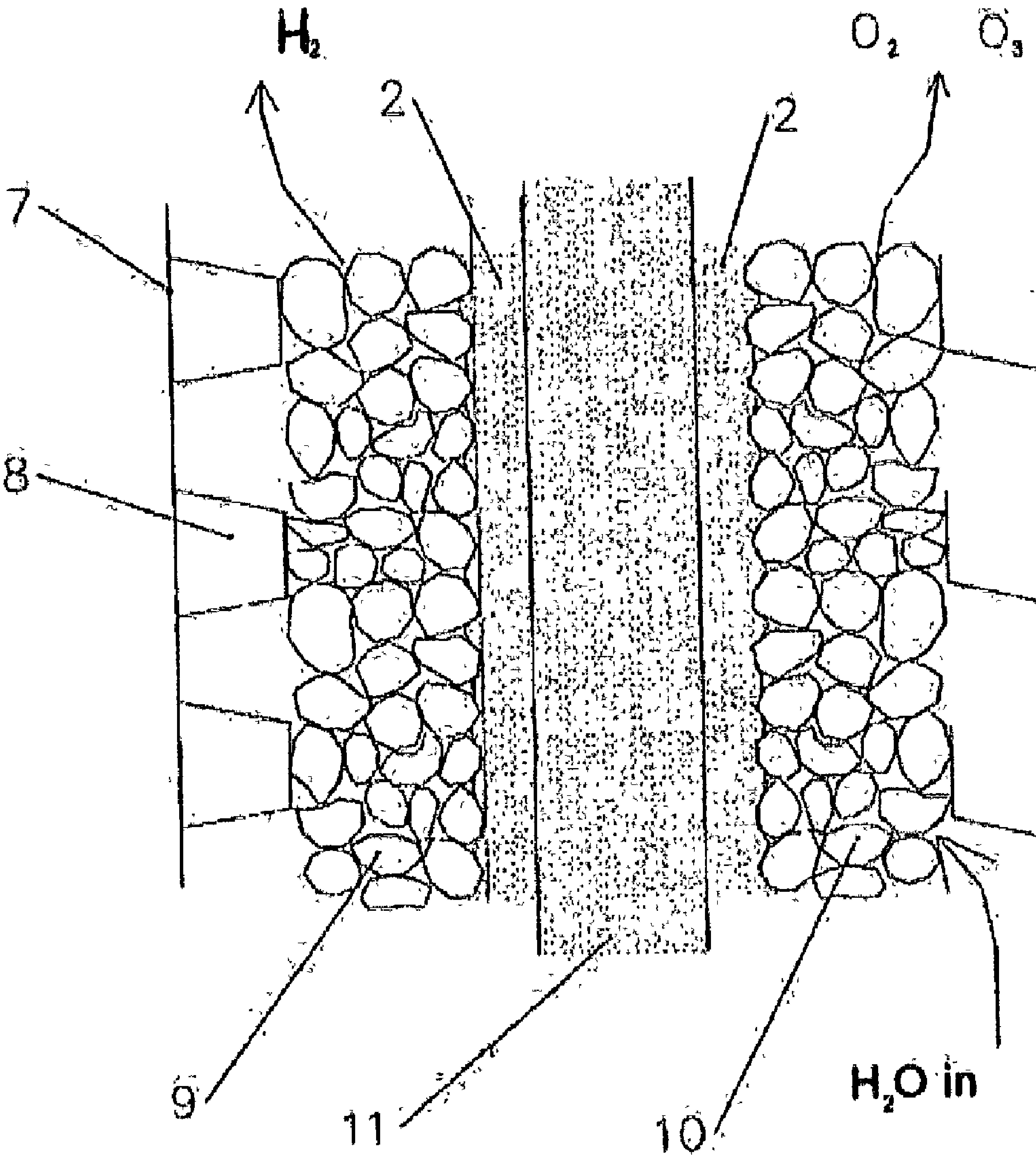

Fig. 6

ELECTROCHEMICAL REACTING ELECTRODE, METHOD OF MAKING, AND APPLICATION DEVICE

RELATED APPLICATIONS

[0001] Priority is claimed to U.S. Provisional Patent Application Ser. No. 60/314,064, filed Aug. 22, 2001 and U.S. Provisional Patent Application Ser. No. 60/383,880, filed May 29, 2002.

FIELD OF THE INVENTION

[0002] The present invention refers to methods for the manufacture of gas-diffusion electrodes having porous conducting substrate on which a layer of ion-exchange polymer is applied—in particular, to methods for introducing catalyst particles into the electrode structure. The invention may be used for manufacturing electrodes used for fuel cells, water electrolysis, ozone production, as well as electrodes for other electrochemical devices.

[0003] The present invention is also related to the construction and method of production of electrodes for electrochemical reactions, for electrolysis primarily, as well as to the construction of an electrolyzer including such electrodes. The invention may be used for ozone production through decomposition of water by the electrochemical method, and for manufacturing of fuel cells.

BACKGROUND OF THE INVENTION

[0004] The following methods for manufacturing electrodes in which catalyst deposition is carried out by the electrochemical method are known.

[0005] The method for the manufacture of gas-diffusion electrodes offering high catalytic activity and consisting of a gas-permeable layer (substrate) and reactive layer is described in U.S. Pat. No. 5,084,144. Said reactive layer is impregnated with an ion-exchange polymer. Then electrode is placed into an electrolytic bath with a counter-electrode, with said electrolytic bath containing electrolyte with ions of platinum metals (catalysts). When a pulse current passes through the electrolyte, particles of metals are deposited on the surface of the reactive layer in the areas where said reactive layer is in contact with the ion-exchange polymer.

[0006] Another method for the manufacture of gas-diffusion electrode is described in U.S. Pat. No. 6,080,504. According to this method a reactive layer containing ion-exchange resin is produced on a gas-permeable conductive substrate first. The reactive layer is brought in contact with electrolyte containing ions of metal (catalyst). A pulse current is passed through the gas-diffusion electrode and a counter-electrode to deposit particles of metal catalyst on reactive layer.

[0007] Another method for the manufacture of electrodes for electrochemical devices is described in U.S. Pat. No. 5,284,571. According to this method the substrate, the part of which contains proton-conducting material mixed with an electron-conducting material, is produced at first. Said proton-conducting material contains a multitude of acidic functional groups, each of which has a cation capable of substitution. Then said substrate is placed into an electrochemical cell with a counter-electrode and electrolyte. The electrolyte is an aqueous solution that contains complex amino-platinic cations. A voltage sufficient for the deposition of platinum particles in the areas where the proton-conducting material contacts electron-conducting material is then supplied to electrodes.

[0008] Another method for the manufacture of an electrode for fuel cells is described in U.S. Pat. No. 20,020,015, 878. According to this method a substrate is produced out of a mixture of cation-exchange resin and carbon particles. The substrate is then placed for some time in a solution containing cations that contain metal catalyst. After this cations that have adsorbed into cation-exchange resin are reduced in a gaseous hydrogen atmosphere to catalyst metal.

[0009] The method for the manufacture of electrodes described in U.S. Pat. No. 6,258,239 produces a porous conductive substrate is produced. Then a film (which is an ion-conducting polymer) is produced on one side of said substrate. Then a catalyst is deposited on the substrate surface (from electrolyte that contains ions of metal catalyst) by the method of electrochemical reduction by applying controlled pulse voltage between the electrode and a counter-electrode.

[0010] Electrodes in which a layer of ion-exchange polymer (having channel-cluster structure) is applied on said porous conductive substrate are produced by methods described above. Nano-sized particles of metal catalyst are reduced in the channels of said ion-exchange polymer (directly on the substrate) in these electrodes.

[0011] The known methods are characterized by the fact that ions of metal catalyst are contained in the liquid phase of electrolyte in the course of electrochemical deposition of metal catalyst particles. Under the action of electric field and as a result of diffusion processes, these ions of metal catalyst are continuously supplied to the channels of ion-exchange polymer. These circumstances result in the following disadvantages:

> **[0012]** 1) Deposition of metal catalyst on the substrate is non-uniform because the layer of ion exchange polymer on the substrate is uneven. The deposition process is more rapid on those areas of the substrate where the ion-exchange polymer is thinner.
>
> **[0013]** 2) Following completion of the reduction process, a portion of the cation complexes containing metal catalyst remains bound to the layer of ion-exchange polymer. This reduces ion conductivity of the ion-exchange polymer in a finished electrode and adversely affects electrode operating parameters. Removal of bound cations by water is impossible (washing in strong acids is required for the removal of bound cations, which step would make the entire process more expensive).
>
> **[0014]** 3) When ion-exchange polymer does not cover the entire surface of a substrate, catalyst deposition proceeds predominantly on those areas of the substrate surface where said polymer is missing, creating gaps. This phenomenon will result in the production of large metal particles that would not perform catalytic functions effectively.

[0015] Various constructions of electrodes are known, as well as methods of their production and electrolyzers, e.g. for ozone generation.

[0016] Oftentimes the electrodes include of a porous conducting substrate, for instance, of graphite, and a layer of metallic catalyst applied to one of the sides of the substrate. The thin layer of catalyst is applied, as a rule, by spray coating, compression molding, or application of a catalyst-containing colloidal solution with subsequent evaporation of the solution.

[0017] In the U.S. Pat. No. 5,326,444 "Apparatus for electrolytic ozone generation", priority of 9.03.93, IPC C25V 11/00, an electrolyzer for ozone generation is described together with an electrode made of conducting porous material containing catalyst on its surface. The catalyst is applied onto the surface of the porous material by compression molding.

[0018] In the U.S. Pat. No. 5,460,705 "Method and apparatus for electrochemical production of ozone", priority of 13.07.93, IPC C25V 9/00 an electrode is described, including of a porous substrate with catalyst applied to its surface by sintering the metallic catalyst with the substrate.

[0019] According to the patent of Japan No. 3253590 "Production of electrode for,water electrolysis", priority of 2.03.90, IPC C25V 11/16, the formation of the catalyst layer on the porous conducting substrate is done by applying a catalyst-containing liquid and its subsequent evaporation.

[0020] In the patent of Japan No. 3243784 "Production of water electrolyzing electrode", priority of 22.02.90, IPC C25V 11/16, the electrode substrate is made of porous titanium. A viscous platinum-containing solution is applied onto the surface of the substrate. Then the layer is dried, a new layer is applied and dried again. After that the lead catalyst is applied over the layer of platinum.

[0021] The principal disadvantage of the known devices and technologies for ozone production is the low yield of the final product. This is explained, first, by the inefficient utilization of the catalyst, whose activity obviously cannot be 100% due to imperfections of the method of applying the catalyst to the electrode and the resulting non-uniform size of the catalyst particles, and partial catalyst poisoning on contact of the electrode with air. A thicker catalyst layer will only make the process costlier, therefore, optimization of the amount of catalyst with its activity retained becomes a topical technological issue. Second, the yield of ozone is negatively affected by the products of anode and cathode reactions being mixed together. To prevent this from happening, a separating membrane is inserted into the electrolytic cell, made of porous polymer material, which is mechanically strong, resistant to aggressive media, highly conductive and possessing a capacity for selective ion exchange.

[0022] In 1964 the US company "Dupont" patented a method of producing carbon tetrafluoride vinyl esters containing functional sulfo groups capable of exchanging electrostatically bound ions, e.g. those of alkali metals, with the environment. Through polymerization of these esters the most efficient of existing separating membranes for electrochemical installations—"Nafion" membranes (the Russian analog—MF-4SK membranes) were produced. It was found that the selective ion-exchange material with channel-clustered structure that the "Nafion" membranes are made of has an extremely high conductivity—a property of a solid polymer cationic electrolyte (Timonov A. M. "Solid Polymer Electrolytes: Structure, Properties, and Use" (in Russian).—"Sorosovskiy Obrazovatelny Zhurnal", vol. 6, No. 8, 2000, pp. 69-75). The diffusion coefficient of sodium ions in the "Nafion" is comparable to that for the liquid electrolyte based on concentrated water solution of sodium chloride. This means that the "Nafion" membrane can replace liquid electrolyte in the electrolytic cell.

[0023] A solid polymer electrochemical generator of hydrogen and oxygen is known, where electrodes of porous titanium are used, with a "Nafion" membrane—a solid polymer electrolyte between them (Timonov A. M., ibid.). The principle of operation of the known electrolyzer as a hydrogen and oxygen generator is as follows. Distilled water is supplied into the anodic space of the electrolyzer and via the pores of the anode to the electrode/"Nafion" boundary area. Within this boundary area electric oxidation of water takes place, with oxygen release. Oxygen is removed from the reaction zone through the pores of the electrode, and the gas permeability of the "Nafion" prevents oxygen from entering the cathode space and producing an explosive fulminating mixture. Hydrated protons move through the membrane towards the cathode, where they are reduced with the release of gaseous hydrogen. Like oxygen, hydrogen is removed via the cathode pore system into the current supply channels. The process of cathode and anode reactions is enhanced by catalysts introduced over the electrode/"Nafion" boundary area—finely dispersed platinum and iridium oxide (IV) respectively. At that a part of the catalyst applied to the electrode gets into the pores-channels on the "Nafion" surface. The technology makes it possible to reduce the amount of precious metals used to 0.1 mg per 1 cm^2 of the electrode surface, and the thickness of the electrolytic cell to several millimeters. An advantage of the known device is that oxygen for medical purposes (of high degree of purity) can be produced. However, in regard to the catalyst efficiency, this device is not free from disadvantages like those described above.

[0024] The construction of the hydrogen-oxygen fuel cell using the same electrodes and a "Nafion" separating membrane is not much different from that described above. Hydrogen and oxygen are used as fuel for such cells, the reaction on the electrodes goes in the reverse, and its products are water and electric power. However, the efficiency of these cells does not exceed 50%, and the voltage is 0.8 V. This is also explained by the low efficiency of catalyst operation, and, consequently, low efficiency of the process of reaction.

SUMMARY OF INVENTION EMBODIMENTS

[0025] The present invention includes a new and improved method for the manufacture of catalytically active gas-diffusion electrode that is free from disadvantages mentioned above.

[0026] One exemplary embodiment of the present invention consists in the following.

[0027] A blank of an electrode (in the form of conducting porous substrate having a layer of ion-exchange polymer having channel-cluster structure applied onto said substrate) is subjected to the following processing. During the first stage, a portion of the protons in the ion-exchange polymer located on the channel walls of the channel-cluster structure of said polymer are substituted by cations containing a metal catalyst. Said substitution is carried out by ionic exchange. To do this, conducting substrate (with a layer of ion-exchange polymer having channel-cluster structure applied onto it) is kept in a solution (in which cations containing metal catalyst are present) for a certain period of time. Due to diffusion, cations penetrate into the channels of the channel-cluster structure of the layer of the ion-exchange polymer, where they replace a portion of protons of the ion-exchange polymer. During the second stage, cations that now replace protons in the channel-cluster structure of the layer of ion-exchange polymer are reduced electrochemically in a solution of electrolyte that doesn't contain ions of the catalytically active metal. Particles of metal catalyst are deposited on the conducting substrate of the electrode during this reduction. Catalyst is deposited on the substrate only in those locations where the channels of the channel-cluster structure of the layer of the ion-exchange polymer contact the substrate.

[0028] In one exemplary embodiment of this process:

[0029] 1) Catalytic metal is deposited on the substrate only in those locations where the channels of the channel-cluster structure of the layer of the ion-exchange polymer contact the substrate.

[0030] 2) The amount of introduced metal can be easily controlled via the concentration of solution containing cations of catalytic metal and the duration of time the layer of ion-exchange polymer is kept in said solution.

[0031] 3) Ionic conductivity of the ion-exchange polymer, following the reduction of catalyst is not impaired because all cations of catalytic metal get completely reduced, thus freeing the space for protons in the channels of the ion-exchange polymer.

[0032] 4) Excessive consumption of metal catalyst is avoided in this case.

[0033] As a result, an electrode with high ionic conductivity and high electrochemical activity is produced using the minimum amount of catalyst required for the manufacture of said electrode.

[0034] A porous conducting substrate with a layer of ion-exchange polymer from 10 to 30μ in thickness can be used in a specific embodiment of the implementation of this method. The layer of ion-exchange polymer on the porous conducting substrate can be thin and can even have gaps. Particles of catalyst will be reduced on the substrate only in those locations where the channels of the channel-cluster structure of the ion-exchange polymer contact the substrate. They won't be reduced on those areas of the substrate that are not covered with a layer of the ion-exchange polymer.

[0035] Aqueous solutions of complex compounds of metal catalysts (with the concentration of the complex being from 10^{-4} to $5 \cdot 10^{-2}$ mol/l) can be used as solutions containing ions of metal catalysts. Cation halogen-amine complexes containing platinum group metals can be used as complex compounds of catalytic metals. In particular, the cation complex containing platinum $[PtEn_2Cl_2]^{2+}$, cation complex containing ruthenium $[RuEn_2Cl_2]^{+}$, cation complex containing iridium $[IrEn_2Cl_2]^{+}$ (in which En—ethylenediamine $H_2N—CH_2—CH_2—NH_2$), and the cation complex containing platinum $[Pt(NH_3)_4Cl_2]^{2+}$ can be used.

[0036] In addition, cations that are formed as a result of dissociation of salts of catalyst metals in aqueous solutions when the concentration of said salts is from 10^{-4} to $5 \cdot 10^{-2}$ mol/l, can be used as said cations containing catalyst metal.

[0037] In order to enable the electrochemical reduction of only those cations that have replaced protons in the channels of the channel-cluster structure of the layer of the ion-exchange polymer and in order to eliminate the loss of expensive compounds of platinum group metals, the electrode can be washed with water prior to electrochemical reduction with the aim to remove the remnants of aqueous solution containing cations including those cations that have not formed bonds with the ion-exchange polymer.

[0038] Electrochemical reduction can be carried out in an electrolysis bath, using an electrolyte that need not contain cations of catalytic metals—for example, in a bath containing sulfuric acid with concentration 0.05-2 mol/l.

[0039] In order to ensure that the process of electrochemical reduction takes place only on the substrate surface, this process should be carried out at a potential that is less negative than that at which hydrogen is released (reduced) under given conditions. It is necessary to prevent hydrogen release because free hydrogen has the ability to reduce cations anywhere within the cluster structure, not just on the surface of the substrate. A potential difference is applied between a counter-electrode that is placed into the bath for the electrochemical reduction and the electrode upon which catalyst is being deposited. If the difference in potentials is too high, then hydrogen will be released which, in turn, will reduce cations of catalytic metal in any area of the channel-cluster structure of the ion-exchange polymer (i.e. not only on the substrate surface areas where said substrate is in contact with the channels of the channel-cluster structure of the ion-exchange polymer).

[0040] Following the deposition of first particles of metal catalyst, such as platinum, for example, due to change in catalytic properties of newly formed electrode surface, the decrease of the overvoltage of hydrogen may take place. This may lead to the release of hydrogen and speeding up of the reduction of metal due to chemical reduction in addition to electrochemical reduction. If this speedup is not desirable, for example, when we need to conserve the amount of precious metal, the decrease of voltage will stop the hydrogen formation.

[0041] If the electrodes being manufactured require the conducting porous substrate to have hydrophobic properties (for example, electrodes for fuel cells), electrochemical reduction is carried out preferably using direct or pulse current with an effective value of cathodic current density ranging from 15 to 200 mA/cm^2 and at a temperature ranging from 20 to 95° C. for a period of 1 to 2 hours.

[0042] Similarly, when manufacturing electrodes that do not require hydrophobic properties (for example, electrodes for electrolysis devices), said electrochemical reduction is preferably carried out using direct or pulse current with the effective value of cathodic current density ranging from 0.5 to 2 A/cm^2 and at a temperature ranging from 20 to 95° C. for a period of 1 to 2 hours.

[0043] If the goal is to increase catalytic activity and reduce the expensive catalyst material, it is possible to use layer-by-layer deposition of different metals for the manufacture of electrodes.

[0044] When performing layer-by-layer deposition of different metal catalysts on a porous conducting substrate, usually the replacement of a portion of protons of ion-exchange polymer in the channels of the channel-cluster structure with cations containing another metal catalyst and subsequent electrochemical reduction of these cations is performed sequentially.

[0045] In particular, first platinum is deposited on the substrate surface, after which iridium is deposited. In this case complex cations $[PtEn_2Cl_2]^{2+}$ are used as platinum-containing cations, and complex cations $[IrEn_2Cl_2]^{+}$ are used as iridium-containing cations. In both cases En represents ethylenediamine—$H_2N—CH_2—CH_2—NH_2$.

[0046] It is also possible to reduce platinum particles followed by lead particles, or vice versa. In this case said complex cations of platinum—$[PtEn_2Cl_2]^{2+}$—are reduced first, and electrochemical reduction of platinum is preferably carried out at a cathodic density ranging from 15 to 200 mA/cm^2 and at a temperature ranging from 20 to 95° C. during a period of 1 to 2 hours. Cations that are formed as a result of dissociation in an aqueous solution of lead (II) nitrate or solution of lead (II) acetate are used as lead cations, and electrochemical reduction of lead is carried out at a cathodic density ranging from 10 to 300 mA/cm^2 and at a temperature ranging from 20 to 95° C. for a period of 1 to 2 hours.

[0047] Further embodiments of the present invention aimed at producing an electrode whose construction would be free of the above-listed disadvantages to make it possible to avoid the low-catalysis efficiency and a high contact resistance in the electrode/electrolyte boundary area, and at producing a high-performance electrolyzer incorporating this electrode.

[0048] An electrode for electrochemical reactions according to the principles of the present invention includes a porous conducting substrate, a layer of a polymer ion-exchange membrane having a channel-clustered structure, formed on the surface of the above-mentioned substrate, and particles of a metallic catalyst fixed to the above-mentioned substrate in locations where the latter conjugates with the channels of the channel-clustered structure of the said layer of the ion-exchange membrane.

[0049] Carbon or titanium may be used as a material for the porous conducting substrate of the electrode.

[0050] A layer of the ion-exchange membrane can be made, for example, out of a solid polymer electrolyte, in particular, of "Nafion" carbon tetrafluoride polymer. The thickness of the ion-exchange membrane layer can be from 10 to 30 μm.

[0051] The catalyst particles can include metals of the platinum series, e.g. platinum or iridium, or ruthenium. The composition of the metallic catalyst can include different metals at the same time, e.g. platinum and iridium, platinum and lead, in proportions by weight varying from 1:5 to 1:15. With that, the particles of different metals may be either randomly located in the catalyst layer, or in successive layers, e.g. lead layer over platinum layer.

[0052] One exemplary method of electrode manufacturing includes the following stages:

[0053] 1. A layer of the polymer ion-exchange membrane having a channel-clustered structure is formed on a porous conducting substrate.

[0054] The layer of the polymer ion-exchange membrane having a channel-clustered structure may be formed in two ways.

[0055] The first way is to apply a layer of the colloidal solution of the oligomer in an organic solvent, for example, isopropanol, onto the porous conducting substrate with subsequent heating until the polymer layer of the ion-exchange membrane is formed. In the case when the "Nafion" oligomer is used to obtain the layer of the polymer ion-exchange membrane, the isopropanol solution of the oligomer in concentration of 8 to 12% by weight is applied to the substrate, and heating of the substrate with the colloidal solution of the oligomer applied to it is done at a temperature of 70 to 100° C. for 1 to 1.5 hours.

[0056] The second way is to apply a layer of the colloidal solution of the polymer in an organic solvent to the porous conducting substrate with subsequent drying by heating until the polymer layer of the ion-exchange membrane with channel-clustered structure is formed. In the case when the "Nafion" polymer is used to obtain the layer of the polymer ion-exchange membrane, the drying of the colloidal solution of the polymer by heating is done at a temperature in the range of 30 to 100° C. for 0.8 to 1.5 hours.

[0057] 2. Embedding and fixing the catalyst in the reaction zone of the electrode are performed, i.e. the formation of the catalyst layer. For this purpose cations of one or different metals are introduced into the channels of the channel-clustered structure by means of ion exchange, which are then reduced electrochemically to produce metallic catalyst particles on the porous surface of the substrate in locations where the channels of the channel-clustered structure of the ion-exchange membrane layer conjugate with the substrate. In order to form a multi-layer catalyst of one or different metals, the above-mentioned process of the catalyst layer formation is repeated in succession.

[0058] Ion exchange (saturation of the membrane with the cations of a metal to be used as catalyst) is effected by letting the substrate with the membrane layer applied to it stay in the water solution of a cationic complex compound of the catalyst to be introduced, or its salt. The conditions of this exposure (concentration of the complex compound or the salt of the metal in the solution, the time of exposure) are determined by the desired surface concentration of the metallic catalyst in the electrode.

[0059] $[PtEn_2Cl_2]^{2+}$, for instance, may be used as a cationic complex compound, where En is ethylenediamine, $H_2N—CH_2—CH_2—NH_2$. Electrochemical reduction of platinum is performed at a current density within the range of 0.5 to 1 A/cm^2 and at a temperature of 70 to 90° C. for 1 to 2 hours. Conditions for introducing ruthenium, or iridium, or a mixture of the platinum series metals, or platinum and lead (in proportion of 1:5 to 1:15 by weight) as catalysts are analogous (at that the particles of different metals will be randomly located within the catalyst layer).

[0060] If different metals enter into the composition of the catalyst, platinum and lead, for example, and it is required that on the electrode the particles of the latter catalyst (i.e. lead) were located over the particles of the former (i.e. platinum), the catalysts are successively introduced in the electrode, i.e. the above-mentioned process of forming the catalyst layer is repeated in succession. For that purpose platinum cations are first introduced into the channels of the channel-clustered layer of the ion-exchange membrane by means of ion exchange, and reduced electrochemically to obtain metallic particles of the catalyst on the porous surface of the substrate in locations where the channels of the channel-clustered structure of the ion-exchange membrane layer conjugate with the substrate. Further on lead cations are introduced into the channels of the channel-clustered layer of the ion-exchange membrane by means of ion exchange, and reduced electrochemically to obtain metallic particles of lead on the surface of the particles of the first catalyst—platinum.

[0061] $[PtEn_2Cl_2]^{2+}$ is used as a cationic complex compound for obtaining the first metallic catalyst. Electrochemical reduction of platinum is performed at a current density within the range of 0.5 to 1 A/cm^2 and at a temperature of 70 to 90° C. for 1 to 2 hours.

[0062] In the case of lead its water-soluble nitrate can be used. Electrochemical reduction of lead is performed at a current density within the range of 0.1 to 0.3 A/cm^2 for 1 to 2 hours.

[0063] If for successive formation of the catalyst layers metals of platinum series or ruthenium are used, the course of action is as follows. For instance, if platinum is used as the first catalyst metal, and iridium is used as the second catalyst metal, then in order to obtain the above-mentioned first catalyst during the introduction of platinum cations, the complex compound of platinum $[PtEn_2Cl_2]^{2+}$ is used in ion exchange, where En is ethylenediamine, $H_2N—CH_2—CH_2—NH_2$, at that the electrochemical reduction of platinum is performed at a current density within the range of 0.5 to 1 A/cm^2 and at a temperature of 70 to 90° C. for 1 to 2 hours, while in order to obtain the above-mentioned second catalyst during the introduction of iridium cations the complex compound of iridium $[IrEn_2Cl_2]^{2+}$ is used in ion exchange, where En is ethylenediamine, $H_2N—CH_2—CH_2—NH_2$, at that the electrochemical reduction of platinum is performed at a current density within the range of 0.5 to 1 A/cm^2 and at a temperature of 70 to 90° C. for 1 to 2 hours. Conditions for obtaining multi-layer catalysts with any other combination of metals of platinum series or their combination with ruthenium are similar.

[0064] The electrolyzer according to the present invention includes an anode and a cathode, either of those made in the form of the electrode according to any of the above-listed embodiments, i.e. having a porous conducting substrate, a layer of the polymer ion-exchange membrane of channel-clustered structure formed on the surface of the above-mentioned substrate, and metallic catalyst particles fixed to the above-mentioned substrate in locations where the latter conjugates with the channels of the channel-clustered structure of the above-mentioned layer of the ion-exchange membrane, also the electrolyzer includes a separating membrane installed between the anode and the cathode, the above-mentioned separating membrane made out of a polymer ion-exchange material having a channel-clustered structure. The layer of the ion-exchange membrane of the anode and the cathode conjugates with the separating membrane.

[0065] The exemplary electrolyzer construction includes that both anode and cathode having principally identical catalyst layers.

[0066] The thickness of the layer of the separating membrane should not exceed 100 μm. The layer of the electrode ion-exchange membrane and the separating membrane may be made of the same material, for instance, of a solid polymer electrolyte, specifically, of "Nafion" carbon tetrafluoride polymer.

[0067] Some advantages of the present electrode invention are:

> **[0068]** obtaining stable nano-sized catalyst particles on the substrate surface; the size of the particles and their stability are determined by the fact that the electrochemical process of the reduction of the complex is localized in the channels of the membrane layer;
>
> **[0069]** a reliable contact between the catalyst particles and the electrode substrate, which is achieved by using the electrochemical method of catalyst formation;
>
> **[0070]** optimization of the amount of the catalyst provided via the formation of the catalyst in the channel-clustered structure of the membrane, i.e. right in the place where the electrochemical processes will be going on;
>
> **[0071]** efficient use of the catalyst owing to the fact that the catalyst formation takes place in an area where highly-active metal particles are out of contact with air and with substances capable of poisoning the catalyst;
>
> **[0072]** when using the present electrode embodiment in an electrolyzer, a low electric contact resistance is ensured, as two homogeneous materials are joined in the electrode/electrolyte boundary area. This would provide a high-performance electrolyzer, owing to the chemical modification of the electrode which resulted in the optimization of the catalyst localization on the electrode, the catalyst amount and activity, and owing to lower contact resistance in the boundary area between the materials of the surface layer of the electrode and the solid electrolyte (the separating membrane), which are homogeneous in composition and structure.

[0073] Distinctive features of the present electrode include its surface layer of the polymer ion-exchange membrane having a unique channel-clustered structure, the composition of the catalyst and the location of the catalyst in the zone of electrochemical reaction—i.e. in the area where the substrate and the surface layer (membrane) are conjugated.

[0074] Distinctive features of the present method include process steps and conditions for producing the surface layer (membrane) of the electrode, introducing and localizing the catalyst, catalyst composition and the nature of the membrane.

[0075] Distinctive features of the device—electrolyzer—include the unique anode and cathode, the electrolyte, conjugation of the modified electrode with the electrolyte.

BRIEF DESCRIPTION OF THE DRAWINGS

[0076] The invention claimed herein is illustrated by the following Figures.

[0077] **FIG. 1** shows the structure of an electrode, where: **1**—porous conducting substrate, **2**—layer of ion-exchange polymer.

[0078] **FIG. 2** schematically shows the segment of an electrode with catalyst consisting of particles of one substance, where: **3**—channels of the channel-cluster structure of layer **2** of ion-exchange polymer, **4**—nano-sized particles of catalyst.

[0079] **FIG. 3** schematically shows the segment of an electrode with a catalyst consisting of particles of two substances, which are applied layer-by-layer one after another, where: **5**—nano-sized particles of one catalyst, **6**—nano-sized particles of another catalyst.

[0080] **FIG. 4** shows the characteristics of catalytic activity of electrodes made by a method disclosed herein.

[0081] **FIG. 5** shows a group of volt-ampere characteristics of an exemplary embodiment of an electrolyzer that includes electrodes made by a method disclosed herein.

[0082] **FIG. 6** presents structural layout of an ozone-producing electrolyzer that includes the principles of the present invention.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS OF THE INVENTION

[0083] Gas-diffusion electrodes (see **FIG. 1**) comprising porous conducting substrate **1** with a layer **2** of ion-exchange polymer with a channel-cluster structure and layer **2** applied onto said substrate such electrodes are used in various applications—e.g. for fuel cells, electrolysis of water, and ozone production. Porous carbon or porous titanium can be used as the material for the porous conducting substrate. Depending on the application purpose of the electrode, the porous conducting substrate may be required to have hydrophobic properties. This can be achieved for example by introducing water repellant into the substrate material. Fluorocarbon polymer sold under the trademark "Nafion", owned by E. I. DuPont de Nemours and Company Corporation, can be used as an ion-exchange polymer. To ensure effective operation of an electrode, nano-sized particles of metal catalyst should be present in the areas where porous conducting substrate is in contact with channels of the layer of ion-exchange polymer.

[0084] In the general case a method according to the present invention is embodied in the following manner. A blank which consists of a porous conducting substrate with a layer of ion-exchange polymer from about 10 to 30 μm in thickness, is first submerged in a solution that contains cations of catalytic metal. Cations of catalytic metal are produced by dissolving complex compounds of catalytic metals or salts of catalytic metals. The cations diffuse in the electrolyte, penetrate into the channels of the ion-exchange polymer and replace protons in the ion-exchange polymer (in said channels) by ion exchange. Then cations in the channels of the ion-exchange polymer that have replaced the protons are reduced electrochemically. In order to ensure that only these cations are reduced, the reduction process is carried out in a solution that does not contain cations of the catalytic metal. For example, the reduction can be carried out in a bath containing an acid solution. In order to remove cations that are not attached to the ion-exchange polymer by way of ion exchange and proton replacement, including those in the channels, the layer of polymer and the substrate can be washed in water prior to the reduction step. As a result of electrochemical reduction of cations, nano-sized particles of catalytic metal are deposited on those substrate areas, which make contact with the channels of the channel-cluster structure of the ion-exchange polymer (see **FIG. 2**). Platinum group metals (in particular, platinum, ruthenium, iridium and lead) may be used as catalytic metals.

[0085] In order to ensure that the process of electrochemical reduction takes place only on the substrate surface, this process should be carried out at a potential that is less negative than that at which hydrogen is released (reduced) under given conditions. It is necessary to prevent hydrogen release because free hydrogen has the ability to reduce cations anywhere within the cluster structure, not just on the surface of the substrate.

[0086] The following cation complexes are suitable for reducing the catalyst under said conditions that prevent hydrogen release: complex compound of platinum $[PtEn_2Cl_2]Cl_2$, complex compound of ruthenium $[RuEn_2Cl_2]Cl$, complex compound of iridium $[IrEn_2Cl_2]Cl$, where En—is ethylenediamine H_2N—CH_2—CH_2—NH_2, complex compound of platinum $[Pt(NH_3)_4Cl_2]Cl_2$, and also aqua-ions of lead.

EXAMPLE 1

[0087] Manufacture of a Gas-diffusion Electrode with a Porous Conducting Substrate Having Hydrophobic Properties.

[0088] A blank (consisting of a substrate with hydrophobic properties and a layer of ion-exchange polymer) is placed in an aqueous solution of one of the following complex compounds: complex compound of platinum $[PtEn_2Cl_2]Cl_2$, complex compound of ruthenium $[RuEn_2Cl_2]Cl$, complex compound of iridium, or complex compound of platinum $[Pt(NH_3)_4Cl_2]Cl_2$ with the concentration being within the range from 10^{-4} to $5 \cdot 10^{-2}$ mol/l. After said blank has been kept in said solution for a time period ranging from several minutes to 10 hours, depending upon the particle size desired, it should be washed in distilled water.

[0089] Electrochemical reduction of the catalyst particles can be performed in a cell with solid electrolyte or liquid electrolyte. When reduction is carried out in liquid electrolyte (e.g. a solution of sulfuric acid of concentration from 0.05 to 2 mol per liter), an electrolysis cell with electrolyte (into which both said electrode blank and counter-electrode are submerged) is used. In addition to sulfuric acid solutions, solutions of salts, e.g. sodium sulfate of the same molar concentration, can be used as electrolyte.

[0090] When reduction is carried out in a cell with solid polymer electrolyte, an electrolysis cell is used, in which said electrode blank and counter-electrode are separated by a membrane made of proton-exchange polymer (e.g. Nafion 117).

[0091] Electrochemical reduction is carried out using direct or pulse current with the effective value of current density ranging from 15 to 200 mA/cm^2 and at a temperature ranging from 20 to 95° C. for a period of about 1 to 12 hours.

[**0092**] **FIG. 4** gives the characteristics of specific activity of catalyst in a hydrogen-oxygen fuel cell made by the proposed technology having the following catalyst loadings: anode—Pt in the amount of 0.01 mg/cm^2, cathode Pt in the amount 0.03 mg/cm^2.

[**0093**] The substrate was carbon fabric (0.5 mm thick), onto which a gas-diffusion layer consisting of carbon and water repellant was applied under pressure. The amount of water repellant used was 10% for the cathode and 15% for the anode. A 5% Nafion solution was spray-coated onto electrode blank surface. Then this solution was dried for a period of 1 hour at a temperature of 70° C. The thickness of the Nafion layer was equal to 15 μm (for cathode) and 30 μm (for anode).

[**0094**] Subsequently electrode blanks were placed in a 0.001 M solution of complex $[PtEn_2Cl_2]Cl_2$ for a period of 20 minutes for the anode, and 60 minutes for the cathode. Reduction was carried out in two stages. During the first stage a 200 mA/cm^2 current was applied for 2 hours for anode and 4 hours for cathode. During the second stage the current was decreased to 50 mA/cm^2 and applied for a period of 4 hours for anode and 6 hours for cathode.

[**0095**] An alternate embodiment of Example 1 includes in the following. A colloid solution of oligomer in an organic solvent with a concentration in the range from 8 to 12% by weight is applied onto a porous electrically conductive substrate made out of porous carbon or titanium. For instance, 0.2 ml of oligomer solution in isopropanol with a concentration of 8.6% by weight is applied onto 1 cm^2 surface of porous carbon or titanium.

[**0096**] Then the substrate with the applied colloid solution is heated up until a polymer layer of an ion-exchange membrane with a channel-clustered structure is formed on the porous surface of the substrate. Said heating is conducted at a temperature in the range from 70 to 100° C. during a period from 1 to 1.5 hours. The thickness of membrane produced following the thermal treatment of the electrode lies within 10-30 μm. Produced membrane is characterized by high adhesion to substrate.

[**0097**] Polymer layer of an ion-exchange membrane may be produced as a result of the application of a colloid solution of polymer and subsequent drying of this solution. Drying of a colloid solution of polymer is conducted at a temperature from 30 to 100° C. during a period from 0.8 to 1.5 hours. Produced membrane is characterized by high adhesion to substrate.

[**0098**] The next step in the electrode manufacturing process includes in the introduction of a cation complex compound into the channels of a channel-clustered structure of a layer of an ion-exchange membrane. One can also introduce a mixture of cation complex compounds (for example, compounds based on platinum and iridium).

[**0099**] $[PtEn_2Cl_2]^{2+}$ is used as a cation complex for the purpose of deposition of platinum catalyst on a substrate. Cation complex compound is introduced into a membrane in an aqueous solution of the source complex $[PtEn_2Cl_2]^{2+}$ with a concentration of 10^{-3} mole/l. The final concentration of platinum catalyst is determined by the period during which an electrode with a membrane stays in platinum complex (this period varies from 20 minutes to 3 hours). For instance, to attain surface concentration of a platinum catalyst equal to 10^{-5} g/cm^2, one would have to hold a substrate with a membrane layer in said solution for a period of one hour.

[**0100**] Electrochemical reduction of platinum is carried out with current density being in the range from 0.5 to 1 A/cm^2 and at a temperature from 70 to 90° C. during a period from 1 to 2 hours.

[**0101**] The steps of the introduction of a cation complex compound and electrochemical reduction of a metal catalyst may be repeated several times.

EXAMPLE 2

[**0102**] Manufacture of a Gas-diffusion Electrode with a Porous Conducting Substrate that Does Not Have Hydrophobic Properties.

[**0103**] A blank (consisting of a substrate and a layer of ion-exchange polymer) is placed in an aqueous solution of one of the complex compounds listed in Example 1. Replacement of a portion of the protons on the walls of the channel-cluster structure of the ion-exchange polymer with cations of the complex compound is performed in the same manner as in Example 1.

[**0104**] Electrochemical reduction of catalyst particles is carried out in liquid electrolyte using direct or pulse current. The effective value of current density ranges from 0.5 to 2 A/cm^2 at a temperature ranging from 20 to 95° C. for a period of 1 to 2 hours.

[**0105**] **FIG. 5** shows the volt-ampere characteristics of an electrolyzer, in which electrodes manufactured by the described technology were employed. Curve **1** was obtained with a surface concentration of platinum catalyst equal to 10 μg/cm^2 for the cathode and 20 μg/cm^2 for the anode. Curve **2** was obtained with a surface concentration of platinum catalyst equal to 20 μg/cm^2 for the cathode and 40 μg/cm^2 for the anode. Curve **3** was obtained with a surface concentration of platinum catalyst equal to 40 μg/cm^2 for the cathode and 80 μg/cm^2 for the anode. The thickness of the ion-exchange polymer layer was 100 μm. Tt can be seen from the graphs that acceptable densities of electrolysis current at low values of voltage are attained using electrodes having low loadings of a catalyst.

[**0106**] Plates of porous titanium were used as electrodes. A layer of ion-exchange polymer was applied by spray-coating 5% Nafion solution onto the electrode blank surface. Then this solution was dried for a period of 1 hour at a temperature of 70° C. Subsequently electrode blanks were placed in a 0.001 M solution of complex $[PtEn_2Cl_2]Cl_2$ for a period of 15 minutes (at a concentration of 10 μg/cm^2), 30 minutes (at a concentration of 20 μg/cm^2), 60 minutes (at a concentration of 40 μg/cm^2), and 120 minutes (at a concentration of 80 μg/cm^2). Reduction was carried out using 1 A/cm^2 current for a period of 1 hour at a temperature of 35° C.

EXAMPLE 3

[0107] Manufacture of a Gas-diffusion Electrode Having a Layer-by-layer Arrangement of Platinum and Lead Catalyst Layers

[0108] Catalyst particles may include of two and more metals. **FIG. 3** shows a catalyst including of platinum particles **5** and lead particles **6**. In this case the proportion of platinum and lead by weight will be in the range from 1:5 to 1:15. Particles **5** and **6** of the catalyst also make electrical contact with conducting substrate **1** at the junctures of conducting substrate **1** with channels **3** of the channel-clustered structure of layer **2** of the ion-exchange membrane.

[0109] The steps required for application of platinum particles onto the substrate are similar to those described in Example 2. Lead cations from an aqueous solution of lead (II) nitrate salt were used in the subsequent steps. Electrochemical reduction of nano-sized crystalline particles of lead was performed using a current density ranging from 10 to 300 mA/cm^2 at a temperature ranging from 20 to 95° C. for a period of 1 to 2 hours.

[0110] Electrodes for an electrochemical ozonizer were manufactured by the method claimed herein. The loading of platinum catalyst on the cathode was equal to 0.01 mg/cm^2. The anode was made using two layers of catalyst. The layer immediately adjacent to the substrate was platinum at a loading of 0.01 mg/cm^2. The next layer, formed above the platinum layer, was lead at a loading of 0.05 mg/cm^2. Preparation of the electrode and application of the layers was the same as those described in Example 2. Then anode blanks were placed in a 0.2 M aqueous solution $Pb(NO_3)_2$ for a period of 1 hour. Electrochemical reduction of lead to achieve a surface concentration of 50 μg/cm was performed using a current density with an effective value equal to 100 mA/cm^2 for a period of 2 hours. When an electrode is used as electrolyzer anode, oxidation of lead to lead (IV) oxide was performed. A catalytic layer of □-modification of lead dioxide (oxidation mode was as follows: current density—150 mA/cm^2, duration—1 hour) was formed on the electrode surface during this process. A membrane made of Nafion 117 was installed in the ozonizer between the electrodes. An assembly (consisting of electrodes and membrane) with an active area equal to 7 cm^2, with the value of current equal to 2 A and voltage equal to 4 V produced a concentration of ozone in water that was no less than 0.5 mg/l with the flow rate of water equal to 2 liters per minute.

[0111] In an alternate embodiment of Example 3, following the reduction of metal platinum, the following steps are to be performed. At first, lead cations Pb^{2+} was introduced into a channel-clustered structure of a polymer using the ion exchange method for this purpose (for example, implantation of cations was carried out from 0.2 ml of an aqueous solution of $Pb(NO_3)_2$ during a period from 20 minutes to 2 hours), after which step the electrochemical reduction of catalyst cations on electrode surface is performed (said reduction is accompanied by the production of metal lead deposits of nano size with a surface concentration from 10^{-5} to 10^{-4} g/cm^2). The reduction was carried out in an electrolytic cell with current density being of the order of 0.1 A/cm^2 during a period of approximately 2 hours.

[0112] Electrolyzer Embodiment

[0113] A construction of an electrolyzer is shown in **FIG. 6**. A device for ozone production includes of two plates **7** having grating-type elements **8** intended for supplying water and removing gas. Plates **7** squeeze together cathode **9** and anode **10**, between which separating membrane **11** is placed (this separating membrane is a solid polymer electrolyte—for example, of "Nafion" type). There is a layer of polymer ion-exchange membrane **2** on those surfaces of cathode **9** and anode **10** that face membrane **11**. This layer of polymer ion-exchange membrane **2** serves as a carrier for particles of metallic catalyst.

[0114] A specific feature of the construction of described electrolyzer intended for ozone production includes in the fact that a gap between cathode **9** and anode **10** doesn't exceed 100 μm, which fact makes it possible to create electric field of high strength in the inter-electrode space. Such field strength is comparable with the conditions for ozone production in a corona discharge. It facilitates the weakening of bonds in an oxygen molecule which fact results in the increase in ozone production efficiency.

[0115] Thus, the suggested construction of the device enables one to attain greater yield of ozone as compared to other known constructions of ozone producing devices. The use of electrodes according to the present invention allows one to attain 1% output of ozone (current output) at a room temperature, and the use of the combined catalyst allows one a to attain 4-5% output of ozone (current output) at a room temperature.

[0116] Practical implementation of the inventions disclosed herein goes beyond specific examples given above. It will be apparent that none of the figures are necessarily drawn to scale. Other and further modification, enhancements, and changes can be made to the herein disclosed embodiments without departing from the spirit and scope of the present invention. The selection of materials can be standard and are well known in the art.

1. An electrode for electrochemical reactions comprising a porous conducting substrate, a polymer ion-exchange membrane layer applied on said substrate and having a channel-clustered structure, and metallic catalyst particles attached to said substrate in the locations wherein said particles conjugate with the channels of the channel-clustered structure of said polymer ion-exchange membrane layer.

2. The electrode of claim 1, wherein the porous conducting substrate is comprised of carbon material.

3. The electrode of claim 1, wherein the porous conducting substrate is comprised of titanium material.

4. The electrode of claim 1, wherein the layer of ion-exchange membrane is comprised of solid polymer electrolyte.

5. The electrode of claim 4, wherein said solid polymer electrolyte comprises "Nafion" carbon tetrafluoride.

6. The electrode of claim 4, wherein said solid polymer electrolyte comprises MF-4SK.

7. The electrode of claim 1, wherein the thickness of the layer of the polymer ion-exchange membrane is from about 10 to 30 μm.

8. The electrode of claim 1, wherein the particles of the metallic catalyst include of platinum series metals, for example, platinum or iridium, or ruthenium.

9. The electrode of claim 1, wherein the composition of metallic catalyst includes different metals of platinum series.

10. The electrode of claim 9, wherein the particles of different metals are randomly distributed in the catalyst layer.

11. The electrode of claim 9, wherein the catalyst layer is formed out of particles of different metals in such a manner that a sublayer out of particles of one metal alternates with a sublayer out of particles of another metal thus producing a multilayer catalyst.

12. The electrode of claim 1, wherein the metallic catalyst includes platinum and lead in the proportion from 1:5 to 1:15 (by weight).

13. The electrode of claim 12, wherein the particles of platinum and lead are randomly distributed in the catalyst layer.

14. The electrode of claim 12, wherein the catalyst layer is formed out of particles of platinum and lead in such a manner that a sublayer out of platinum particles alternates with a sublayer out of lead particles thus producing a multilayer catalyst.

15. A method for manufacturing the electrode electrode for electrochemical reactions comprising a porous conducting substrate, a polymer ion-exchange membrane layer applied on said substrate and having a channel-clustered structure, and metallic catalyst particles attached to said substrate in the locations wherein said particles conjugate with the channels of the channel-clustered structure of said polymer ion-exchange membrane layer, the method comprising forming polymer ion-exchange membrane layer with a channel-clustered structure on the porous conducting substrate, thereafter forming the catalyst layer by introducing cations of one or several different metals into the channels of the channel-clustered structure of the layer of ion-exchange membrane using the ion-exchange method, after which electrochemical reduction of said cations is performed with the aim to form metallic particles on the porous surface of the substrate in the locations where said substrate conjugates with the channels of the channel-clustered structure of the ion-exchange membrane layer; with said process of forming the catalyst layer repeated several times to obtain a multilayer catalyst out of one metal or at least two different metals.

16. The method of claim 15, wherein the layer of polymer ion-exchange membrane with channel-clustered structure is produced by applying a layer of the colloid solution of an oligomer in an organic solvent onto the porous conducting substrate and then heating it up until a polymer layer of ion-exchange membrane with a channel-clustered structure is formed.

17. The method of claim 16, wherein a colloid solution of oligomer "Nafion" in isopropanol with the concentration from 8 to 12% by weight is used and the substrate with the applied colloid solution of the oligomer is heated up to 70-100° C. during a period of 1-1.5 hours.

18. The method of claim 15, wherein the polymer layer of the ion-exchange membrane with channel-clustered structure is produced by applying a layer of the colloid solution of a polymer in an organic solvent onto the porous conducing substrate and then drying it up via heating until a polymer layer of ion-exchange membrane with a channel-clustered structure is formed.

19. The method of claim 18, wherein a colloid solution of polymer "Nafion" is used as a polymer and the drying of the colloid solution layer of said polymer is performed at a temperature from 30 to 100° C. during a period of 0.8-1.5 hours.

20. The method of claim 15, wherein the ion exchange during the formation of a catalyst layer is performed by holding the substrate with the applied membrane layer in an aqueous solution of a salt or a complex compound of at least one metal which was selected as a catalyst.

21. The method of claim 20, wherein said complex compound of a metal is represented by the complex compound of platinum [PtEn2Cl2]2+, where En is ethylenediamine, H2N—CH2—CH2—NH2.

22. The method of claim 20, wherein said complex compound of a metal is represented by the complex compound of ruthenium—[RuEn2Cl2]2+, where En is ethylenediamine, H2N—CH2—CH2—NH2.

23. The method of claim 20, wherein said complex compound of a metal is represented by the complex compound of iridium [IrEn2Cl2]2+, where En is ethylenediamine, H2N—CH2—CH2—NH2.

24. The method of claim 20, wherein said complex compound of a metal is represented by a mixture of complex compounds of platinum [PtEn2Cl2]2+ and iridium [IrEn2Cl2]2+, where En is ethylenediamine, H2N—CH2—CH2—NH2.

25. The method of claim 20, wherein said complex compound of a metal and salt of a metal is represented by the complex compound of platinum [PtEn2Cl2]2+, where En is ethylenediamine, H2N—CH2—CH2—NH2, and nitrate of lead, respectively.

26. The method of claim 15, wherein, in case the cations of platinum are introduced for the purpose of the formation of the catalyst layer, platinum is electrochemically reduced at the current density of 0.5-1 A/cm2 and at a temperature of 70-90° C. during a period from 1 to 2 hours.

27. The method of claim 15, wherein, in case the cations of ruthenium are introduced for the purpose of the formation of the catalyst layer, ruthenium is electrochemically reduced at the current density of 0.5-1 A/cm2 and at a temperature of 70-90° C. during a period from 1 to 2 hours.

28. The method of claim 11, wherein, in case the cations of iridium are introduced for the purpose of the formation of the catalyst layer, iridium is electrochemically reduced at the current density of 0.5-1 A/cm2 and at a temperature of 70-90° C. during a period from 1 to 2 hours. The method of claim 15, wherein, in case the cations of platinum and lead are introduced for the purpose of the formation of a mixed platinum-lead catalyst layer, platinum and lead are electrochemically reduced at the current density of 0.5-1 A/cm2 and at a temperature of 70-90° C. during a period from 1 to 2 hours.

29. The method of claim 15, wherein, in case the cations of platinum and iridium are introduced for the purpose of the formation of a mixed platinum-iridium catalyst layer, platinum and iridium are electrochemically reduced at the current density of 0.5-1 A/cm2 and at a temperature of 70-90° C. during a period from 1 to 2 hours.

30. The method of claim 15, wherein, in case the catalyst layers are formed consecutively from different metals, platinum is used as a metal for the first catalyst and lead is used as a metal for the second catalyst.

31. The method of claim 30, wherein the complex compound of platinum [PtEn2Cl2]2+, where En is ethylenediamine, H2N—CH2—CH2-NH2, is used in the ion exchange during the introduction of platinum cations for the production of said first catalyst; with the electrochemical reduction of platinum performed at the current density of 0.5-1 A/cm2 and at a temperature of 70-90° C. during a period from 1 to 2 hours; while nitrate of lead is used in the ion exchange during the introduction of lead cations for the production of said second catalyst; with the electrochemical reduction of lead performed at the current density of 0.1-0.3 A/cm2 and at a temperature from 20 to 95° C. during a period from 1 to 2 hours.

32. The method of claim 15, wherein, in case the catalyst layers are formed consecutively from different metals, platinum is used as a metal for the first catalyst and iridium is used as a metal for the second catalyst.

33. The method of claim 32, wherein the complex compound of platinum [PtEn2Cl2]2+, where En is ethylenediamine, H2N—CH2—CH2—NH2, is used in the ion exchange during the introduction of platinum cations for the production of said first catalyst; with the electrochemical reduction of platinum performed at the current density of 0.5-1 A/cm2 and at a temperature of 70-90° C. during a period from 1 to 2 hours; while the complex compound of iridium [IrEn2Cl2]2+, where En is ethylenediamine, H2N—CH2—CH2—NH2, is used in the ion exchange during the introduction of iridium cations for the production of said second catalyst; with the electrochemical reduction of iridium performed at the current density of 0.5-1 A/cm2 and at a temperature of 70-90° C. during a period from 1 to 2 hours.

34. An electrolyzer comprising two electrodes—anode and cathode, each of which is made in accordance with any of claims **1-14** and each of which has (i) a porous conducting substrate, (ii) a layer of a polymer ion-exchange membrane with a channel-clustered structure with said layer formed on the surface of said substrate, and (iii) metallic catalyst particles attached to said substrate in the spots where the latter conjugates with the channels of channel-clustered structure of said polymer ion-exchange membrane layer; and said electrolyzer further comprising a separating membrane installed between the anode and cathode, with said separating membrane being made out of polymer ion exchange material having a channel-clustered structure, and with a layer of the ion exchange membrane formed on the surface of the anode and cathode being conjugated with the separating membrane.

35. The electrolyzer of claim 34, wherein the anode and cathode have identical catalyst layers.

36. The electrolyzer of claim 34, wherein the thickness of the separating membrane does not exceed 100 μm.

37. The electrolyzer of claim 34, wherein the layer of ion-exchange membrane applied onto the anode and cathode surfaces and the separating membrane are made out of the same material, for example, out of a solid polymer electrolyte, in particular, "Nafion" carbon tetrafluoride.

38. A method for the manufacture of a gas-diffusion electrode with a porous conducting substrate, onto which an ion-exchange polymer layer is applied, comprising the following steps:

replacement of a portion of the protons of ion-exchange polymer in the channels of the channel-cluster structure of said polymer with cations of metal catalyst (said substitution is performed via ionic exchange),

electrochemical reduction of cations that have replaced protons in the channels of the channel-cluster structure of the ion-exchange polymer layer to particles of metal catalyst on those areas of said substrate where the substrate makes contact with the channels of the channel-cluster structure of the ion-exchange polymer layer.

39. The method of claim 38, wherein a substrate with a layer of ion-exchange polymer of 10 to 30 μm in thickness is used.

40. The method of claim 38, wherein cation complexes of metal catalysts are used as said cations of metal catalysts.

41. The method of claim 40, wherein said complexes of catalytic metals in aqueous solution with concentrations from 10-4 to 5·10-2 mol/l are used.

42. The method of claim 40, wherein cation halogen-amine complexes of platinum group metals are used as said complexes of catalytic metals.

43. The method of claim 42, wherein the complex compound of platinum—[PtEn2Cl2]2+ (where En—ethylenediamine, H2N—CH2—CH2—NH2)—is used as said cation halogen-amine complex of metal of platinum group.

44. The method of claim 42, wherein the complex compound of ruthenium—[RuEn2Cl2]+, (where En—ethylenediamine, H2N—CH2—CH2—NH2)—is used as said cation halogen-amine complex of metal of platinum group.

45. The method of claim 42, wherein the complex compound of iridium—[IrEn2Cl2]+, (where En—ethylenediamine, H2N—CH2—CH2—NH2)—is used as said cation halogen-amine complex of metal of platinum group.

46. The method of claim 43, wherein the complex compound of platinum—[Pt(NH3)4Cl2]2+ is used as said cation halogenamine complex of metal of platinum group.

47. The method of claim 38, wherein cations formed as a result of dissociation of aqueous solutions of salts of catalytic metals are used as said cations of catalytic metal.

48. The method of claim 47, wherein the salt concentration of said aqueous solutions of salts of catalytic metals lies within the range of 10-4 to 5·10-2 mol/l.

49. The method of claim 38, wherein said electrode with a layer of ion-exchange polymer is washed in water prior to said electrochemical reduction.

50. The method of claim 38, wherein said electrochemical reduction is carried out in an electrolysis bath, the electrolyte of which does not contain cations of the catalytic metal.

51. The method of claim 50, wherein said electrochemical reduction is carried out in a bath containing sulfuric acid with a concentration in the range of 0.05 to 2 moles.

52. The method of claim 38, wherein said electrochemical reduction is carried out at a difference of potentials that is less than the difference of potentials that leads to the hydrogen release.

53. The method of claim 38, wherein in the case when the substrate has hydrophobic properties, said electrochemical reduction is carried out using direct or pulse current with the effective value of cathodic current density ranging from 15 to 200 mA/cm2 and at a temperature ranging from 20 to 95° C. for a period of 1 to 2 hours.

54. The method of claim 38, wherein in the case when a material that doesn't have hydrophobic properties is used as a material for said substrate, said electrochemical reduction is carried out using direct or pulse current with the effective value of cathodic current density ranging from 0.5 to 2 A/cm2 and at a temperature ranging from 20 to 95° C. for a period of 1 to 2 hours.

55. The method of claim 38, wherein following the reduction of metal particles of one catalyst, the subsequent step of substituting a portion of protons of the ion-exchange polymer in the channels of the channel-cluster structure with cations containing a second metal catalyst is carried out, followed by subsequent electrochemical reduction of these cations to metal particles of another catalyst.

56. The method of claim 55, wherein platinum is deposited onto said substrate first, after which iridium is deposited onto produced platinum layer.

57. The method of claim 56, wherein the cation complex of platinum—[PtEn2Cl2]2+ (where En—ethylenediamine, H2N—CH2—CH2—NH2)—is used as platinum cations, and cation complex—[IrEn2Cl2]+ (where En—ethylenediamine, H2N—CH2—CH2—NH2)—is used as iridium cations.

58. The method of claim 55, wherein platinum is deposited onto said substrate first, after which lead is deposited onto produced platinum layer, or vice versa.

59. The method of claim 58, wherein the cation complex of platinum—[PtEn2Cl2]2+ (where En—ethylenediamine, H2N—CH2—CH2—NH2)—is used as platinum cations, and electrochemical reduction is carried out by using direct or pulse current with the effective value of current density being within the range from 15 to 200 mA/cm2 and at a temperature being within the range from 20 to 95° C. during a period from 1 to 2 hours, and wherein cations formed as a result of dissociation of an aqueous solutions of lead (II) nitrate or lead (II) acetate are used as lead cations, and electrochemical reduction is carried out with the effective value of current density being within the range from 10 to 300 mA/cm2 and at a temperature being within the range from 20 to 95° C. during a period from 1 to 2 hours.

60. A product made by the method of claim 1.

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