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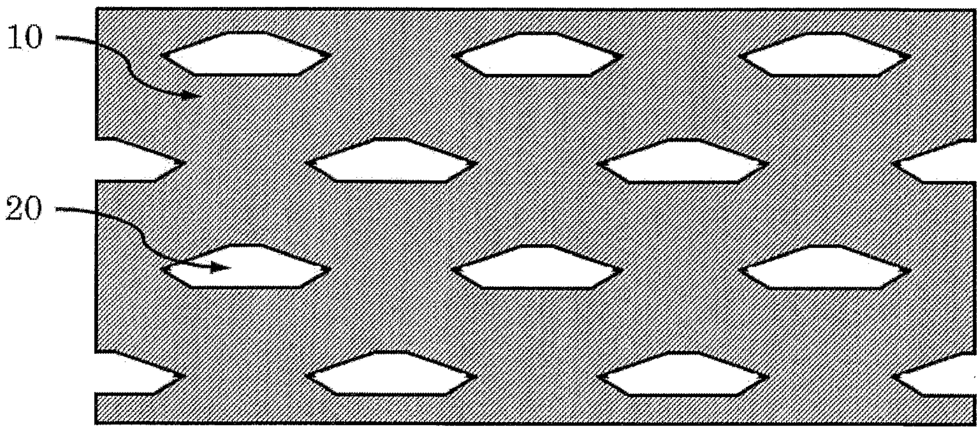
(54) ELECTRODE FOR ELECTROLYSIS, ELECTROLYTIC CELL, ELECTRODE LAMINATE AND METHOD FOR RENEWING ELECTRODE

(57) An electrode for electrolysis including
a conductive substrate formed of a porous metal plate, and
at least one catalyst layer formed on a surface of the conductive substrate, wherein
the electrode for electrolysis has a thickness of more than 0.5 mm and 1.2 mm or less; and
value C, which is obtained by dividing sum B of perimeters of openings of the electrode for electrolysis by opening ratio A of the electrode for electrolysis, is more than 2 and 5 or less.

Figure 2



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Description

Technical Field

[0001] The present invention relates to an electrode for electrolysis, an electrolyzer, an electrode laminate and a method for renewing an electrode.

Background Art

[0002] Sodium chloride electrolysis by ion exchange membrane process is a method for electrically decomposing (electrolyzing) brine by use of an electrode for electrolysis to produce caustic soda, chlorine and hydrogen. In sodium chloride electrolysis by ion exchange membrane process, a technology for maintaining low electrolysis voltage for a long term is required in order to reduce power consumption, in view of environmental load and energy problem.

[0003] To more specifically analyze the breakdown of the electrolysis voltage, it has been found that not only a theoretical requisite electrolysis voltage but also voltages due to resistance of an ion exchange membrane and structure resistance of an electrolyzer, overvoltages of an anode and a cathode serving as electrodes for electrolysis, and voltage due to the distance between an anode and a cathode, are included. If electrolysis is continued for a long term, voltage may sometimes increase due to causes such as impurities contained in brine.

[0004] Of the electrolysis voltages, in order to reduce overvoltage of an anode for generating chlorine, various investigations are carried out. For example, Patent Literature 1 discloses a technique of an insoluble anode, which is formed by coating a titanium substrate with an oxide of a platinum group metal such as ruthenium. This anode is called as DSA (registered trade mark, Dimension Stable Anode). Non Patent Literature 1 describes progress of soda electrolysis technology using DSA.

[0005] DSA has been improved in various ways up to present with a view to improving performance.

[0006] For example, Patent Literature 2 proposes an electrolytic process by moving the surface of a cation exchange membrane facing to an anode to close to an anode, as much as possible, which uses a metallic porous plate having a predetermined thickness, pore diameter and a porosity or an expanded metal having a predetermined thickness, major axis, minor axis and opening ratio. Patent Literature 3 proposes an anode virtually formed of a metallic diamond-shaped mesh and having a predetermined ratios of mesh strands and openings, predetermined intervals of openings in the longitudinal direction (LWD) and the width direction(SWD). Patent Literature 3 discloses that a platinum group metal oxide, magnetite, ferrite, cobalt spinel or a metal oxide mixture can be used as a coating material to be applied on the surface of a metallic mesh having the diamond shape.

[0007] Patent Literature 4 proposes a technique for improving electrolysis performance by using an expanded metal made of titanium or a metallic mesh made of titanium as an anode substrate; controlling the opening ratio and thickness of the anode substrate to fall within predetermined ranges; and controlling a maximum up-and-down height difference of the surface of anode substrate coated with a catalyst to fall within predetermined ranges.

[0008] Patent Literature 5 describes that the voltage of a cell during electrolysis can be reduced by reducing the thickness of an anode by half or less of that of a conventional anode, and controlling the ratios of openings in the longitudinal direction and the lateral direction. Using the electrode (anode), attempts to reduce the amount of impurity gas, i.e., oxygen gas, which is generated by the reaction of hydroxide ions diffused from a cathode chamber through an ion exchange membrane, have been made.

[0009] As described above, reducing thickness of an anode and increasing the opening ratio of an anode substrate is employed as a measure for reducing voltage during electrolysis in the art.

Citation List

Patent Literature

[0010]

Patent Literature 1: Japanese Patent Publication No. 46-021884
Patent Literature 2: Japanese Patent Laid-Open No. 58-130286
Patent Literature 3: National Publication of International Patent Application No. 62-502820
Patent Literature 4: Japanese Patent No. 4453973
Patent Literature 5: International Publication No. WO 2015/108115

Non Patent Literature

[0011] Non Patent Literature 1: "Survey Report on Technology Systematization, the eighth series", written by Aikawa Hiroaki, published by the independent administrative agency, the National Science Museum, March 30, 2007, p32

Summary of Invention

Technical Problem

[0012] However, in conventional anodes such as DSA described in Patent Literature 1, the overvoltage immediately after initiation of electrolysis is high and a certain period is required until overvoltage reaches a low value by activation of a catalyst. Because of this, a loss of power consumption is caused during electrolysis, which is problematic.

[0013] In Patent Literatures 2 to 4, the opening ratio of an expanded metal and intervals of openings in the longitudinal direction and width direction of a mesh are investigated; however, the relationship between the shape of an anode and electrolysis voltage has not been sufficiently investigated and a further reduction of electrolysis voltage has been required. Particularly, an anode having a thin mesh and a high opening ratio is not sufficient in strength from practical point of view, which is also problematic.

[0014] In Patent Literature 5, an approach of reducing the voltage of an anode and oxygen gas generation amount by reducing the thickness of an anode by half of that of a conventional anode is employed. However, in industrial electrolyzers employing an ion exchange membrane, since they are operated by applying pressure from a cathode chamber, if an anode mesh is excessively thin, strength cannot be maintained, with the result that two expanded metal sheets must be used by stacking them one on top of the other. Likewise, in order to satisfy strength of an anode and reduction of electrolysis voltage, a further improvement is required.

[0015] The present invention was attained in order to solve the aforementioned problems. Accordingly, an object of the present invention is to provide an electrode for electrolysis successfully keeping down voltage and power consumption during electrolysis and having practical strength, and provide an electrolyzer equipped with the electrode for electrolysis.

Solution to Problem

[0016] The present inventors conducted intensive studies with a view to solving the above problems. As a result, they found that an electrode for electrolysis successfully keeping down voltage and power consumption during electrolysis and having practical strength can be provided by controlling the thickness of an electrode for electrolysis to fall within a predetermined range and controlling a value, which is obtained by dividing the sum of perimeters of openings of the electrode for electrolysis by the opening ratio of the electrode for electrolysis, to fall within a predetermined range. Based on the finding, they arrived at the present invention. The present inventors further found that the aforementioned problems can be solved by forming the openings of the electrode for electrolysis having a predetermined shape, thereby arriving at the present invention.

[1] An electrode for electrolysis comprising
a conductive substrate formed of a porous metal plate, and
at least one catalyst layer formed on a surface of the conductive substrate, wherein
the electrode for electrolysis has a thickness of more than 0.5 mm and 1.2 mm or less; and
value C, which is obtained by dividing sum B of perimeters of openings of the electrode for electrolysis by opening ratio A of the electrode for electrolysis, is more than 2 and 5 or less.
[2] The electrode for electrolysis according to [1], wherein the opening ratio A is 5% or more and less than 25%.
[3] The electrode for electrolysis according to [1] or [2], wherein center-to-center distance SW of the openings in a minor-axis direction of a mesh is 1.5 or more and 3 or less; and center-to-center distance LW in a major-axis direction of the mesh is 2.5 or more and 5 or less.
[4] The electrode for electrolysis according to any of [1] to [3], wherein the electrode for electrolysis has a thickness of more than 0.5 mm and 0.9 mm or less.
[5] The electrode for electrolysis according to any of [1] to [4], wherein value E represented by the following formula (1) is 0.5 or more

$$E = B/(A \times (SW^2 + LW^2)^{1/2}) \qquad (1).$$

[6] An electrolyzer comprising

an anode chamber comprising, as an anode, the electrode for electrolysis according to any of [1] to [5],
a cathode chamber comprising a cathode, and
an ion exchange membrane isolating the anode chamber from the cathode chamber.

[7] The electrolyzer according to [6], wherein the ion exchange membrane has a projection formed of a polymer constituting the ion exchange membrane on a surface facing the anode.

[8] An electrode laminate comprising
the electrode for electrolysis according to any of [1] to [3] and
a base electrode different from the electrode for electrolysis.

[9] The electrode laminate according to [8], wherein the electrode for electrolysis has a thickness of more than 0.5 mm and 0.65 mm or less.

[10] A method for renewing an electrode, comprising a step of welding the electrode for electrolysis according to any of [1] to [3] on an existing electrode in an electrolyzer.

[11] An electrode for electrolysis comprising
a conductive substrate formed of a porous metal plate, and
at least one catalyst layer formed on a surface of the conductive substrate, wherein
a shape of openings of the electrode for electrolysis is right-and-left symmetric about a first imaginary center line extending in a minor-axis direction of a mesh and up-and-down asymmetric about a second imaginary center line extending in a major-axis direction of the mesh; and
the electrode for electrolysis has a thickness of more than 0.5 mm and 1.2 mm or less.

[12] The electrode for electrolysis according to [11], wherein when the openings each are partitioned in portion a and portion b by the second imaginary center line, a value obtained by dividing area Sa of the portion a by area Sb of the portion b is 1.15 or more and 2.0 or less.

[13] The electrode for electrolysis according to [11] or [12], wherein a value obtained by dividing value St, which is obtained by subtracting a maximum size of the openings in the minor-axis direction of a mesh from center-to-center distance SW of the openings in the minor-axis direction of the mesh, by the SW is 0.4 or more.

Advantageous Effects of Invention

[0017] Owing to the present invention, an electrode for electrolysis successfully keeping down voltage and power consumption during electrolysis and having practical strength, is provided.

Brief Description of Drawings

[0018]

[Figure 1] Figure 1 illustrates a schematic diagram describing the relationship between a sum of perimeters of openings and the opening ratio of an electrode for electrolysis, on the assumption that the electrode for electrolysis and the opening have square shapes.

[Figure 2] Figure 2 illustrates a schematic diagram showing a typical image of a projection plane of an electrode for electrolysis according to the present embodiment of the present invention observed by a microscope.

[Figure 3] Figure 3 illustrates a diagram showing the relationship among center-to-center distance SW of openings in the minor-axis direction, center-to-center distance LW in the major-axis and distance d in the mesh according to the present embodiment based on the schematic view of Figure 2.

[Figure 4] Figure 4 (A) illustrates a schematic view showing a typical shape of an opening of the electrode for electrolysis according to another aspect of the present embodiment of the present invention; Figure 4 (B) illustrates a view showing portion a and portion b of Figure 4 (A); and Figure 4 (C) illustrates a view schematically showing a typical shape of an opening of a conventional electrode for electrolysis.

[Figure 5] Figure 5 illustrates a schematic diagram describing the positional relationship between adjacent openings in the electrode for electrolysis according to another aspect of the present embodiment of the present invention.

[Figure 6] Figure 6 illustrates a schematic sectional view of an electrolyzer according to the present embodiment of the invention.

Description of Embodiments

[0019] Hereinafter, the present embodiment of the present invention for carrying out the invention (hereinafter referred to simply as "the present embodiment") will be more specifically described. The following embodiment, which is just an example for describing the present invention, should not be construed as limiting the present invention to the following contents. The present invention can be carried out by appropriately modifying it within the range thereof.

[0020] The electrode for electrolysis according to a first aspect of the present embodiment (hereinafter simply referred to also as a "first electrode for electrolysis") is an electrode for electrolysis having a conductive substrate formed of a porous metal plate and at least one catalyst layer formed on a surface of the conductive substrate, in which the electrode for electrolysis has a thickness of more than 0.5 mm and 1.2 mm or less; and value C, which is obtained by dividing sum B of perimeters of openings of the electrode for electrolysis by opening ratio A of the electrode for electrolysis, is more than 2 and 5 or less. The first electrode for electrolysis having such a structure can keep low voltage and power consumption during electrolysis and has practical strength. The first electrode for electrolysis can be used as a chlorine generation electrode particularly suitable for sodium chloride electrolysis by ion exchange membrane process.

[0021] The electrode for electrolysis according to a second aspect of the present embodiment (hereinafter simply referred to also as a "second electrode for electrolysis") is an electrode for electrolysis having a conductive substrate formed of a porous metal plate and at least one catalyst layer formed on a surface of the electrode for electrolysis, in which the shape of openings is right-and-left symmetric about a first imaginary center line extending in the minor-axis direction of a mesh and up-and-down asymmetric about a second imaginary center line extending in the major-axis direction of the mesh; and the electrode for electrolysis has a thickness of more than 0.5 mm and 1.2 mm or less. The second electrode for electrolysis having such a structure can keep low voltage and power consumption during electrolysis and has practical strength. The second electrode for electrolysis can be used as a chlorine generation electrode particularly suitable for sodium chloride electrolysis by ion exchange membrane process.

[0022] Hereinbelow, the first electrode for electrolysis and second electrode for electrolysis will be collectively referred to as the "electrode for electrolysis according to the present embodiment".

(Conductive substrate)

[0023] In the electrode for electrolysis according to the present embodiment, the conductive substrate is formed of a porous metal plate and used in almost saturated and highly concentrated brine under a chlorine gas generation atmosphere. Because of this, as a material for the conductive substrate, a corrosion resistant valve metal is preferable. Examples of the valve metal include, but are not particularly limited to, titanium, tantalum, niobium and zirconium. Of the valve metals, titanium is preferable in view of economic efficiency and affinity for a catalyst layer.

[0024] The shape of the conductive substrate is not particularly limited as long as it is a porous flat substrate made of a metal; for example, an expanded metal, a porous plate and a metallic mesh are mentioned as the shape. In the present embodiment, an expanded metal is suitably used. The expanded metal is a processed metal generally prepared by extending a flat plate made of a metal or a metal foil while slitting up by an upper blade and a lower blade to form a mesh, and flattening the mesh up to a desired thickness by applying pressure with e.g., a mill roll. Since continuous hoop processing can be employed, a production efficiency is high. Since disposal loss of a starting plate material is not caused, the expanded metal is economical. In addition, because of a one-body structure, complete electrical conductivity is ensured unlike a metallic mesh and no breakage occurs.

[0025] The electrode for electrolysis according to the present embodiment is constituted by forming at least one catalyst layer on a surface of a conductive substrate as mentioned above. The thickness of the electrode for electrolysis according to the present embodiment is more than 0.5 mm and 1.2 mm or less. If the thickness of the electrode for electrolysis is as thin as 0.5 mm or less, an anode is depressed by pressure applied by an ion exchange membrane due to pressure difference between an anode chamber and a cathode chamber produced during electrolysis and pressure applied by a cathode, with the result that distance between the electrodes increases, and thus, electrolysis voltage increases. In contrast, if the thickness of the electrode for electrolysis is beyond 1.2 mm, an expanded metal having a suitable opening ratio and SW (center-to-center distance SW of openings in the minor-axis direction of a mesh) and LW (center-to-center distance LW of openings in the major-axis direction of the mesh) cannot be obtained in the present embodiment. In the same points of view, the thickness of the electrode for electrolysis is preferably more than 0.5 mm and 1.0 mm or less, more preferably more than 0.5 mm and 0.9 mm or less and further preferably 0.7 mm or more and 0.9 mm or less.

[0026] In first electrode for electrolysis, value C (= B/A), which is obtained by dividing sum B of perimeters of openings of the electrode for electrolysis by opening ratio A of the electrode for electrolysis, is more than 2 and 5 or less, preferably 2.5 or more and 4.5 or less and more preferably 3 or more and 4 or less.

[0027] Opening ratio A herein refers to the ratio (S_B/S_A) of the total area S_B of openings to projected area S_A of either one of the surfaces of the electrode for electrolysis. The total area S_B of openings can be referred to as a sum of projected areas of the region in the electrode for electrolysis where e.g., positive ions and an electrolyte solution are not shut off by the conductive substrate (porous metal plate).

[0028] Sum B of perimeters of openings herein is obtained by individually measuring perimeters Li of openings per unit area of the electrode for electrolysis and summing the perimeters of n openings per unit area ($\sum Li$, i = 1 to n) .

[0029] The relationship between the sum of perimeters of openings and the opening ratio will be described with reference to Figure 1. Note that, in Figure 1, an opening is assumed to have a square shape for convenience sake, although the shape differs from those of openings formed in the electrode for electrolysis according to the present embodiment. As shown in Figure 1 (a), when a single square (2 mm × 2 mm) opening 2 is formed in a square electrode 1 (4 mm × 4 mm), the area of the opening is 4 mm^2; the opening ratio is 25%; and the sum of perimeters of openings is 8 mm. In contrast, as shown in Figure 1 (b), when 4 square (1 mm × 1 mm) openings 3 are formed in the same-shape electrode 1 as above, the area of the openings is 4 mm^2, which is the same as in Figure 1 (a); the opening ratio is 25%, which is the same as in Figure 1 (a); however, the sum of perimeters of the openings is 16 mm, which is larger than in Figure 1 (a). Likewise, when the cases having the same opening ratio are compared, the larger the sum of perimeters of openings, the larger the number of openings. This means, in other words, that as a value, which is obtained by dividing the sum of perimeters of openings by an opening ratio, increases, the number of openings increases. As the number of openings increases, a gas passage diverges. For this reason, the number of retaining air bubbles reduces, which contributes to suppressing of a voltage increase.

[0030] Examples of a method for determining the opening ratio and the sum of perimeters of openings include, but are not limited to:

(I) cutting an electrode for electrolysis into square pieces of 10 cm in length × 10 cm in width, making a copy of the pieces by a copy machine, cutting out openings from the copied paper sheet and measuring weight and perimeter of each of the images cut out above; and

(II) observing either one of the surfaces of an electrode for electrolysis by an image observation apparatus such as a microscope, photographing a projection plane and analyzing the image data.

[0031] A typical image is schematically shown in Figure 2. As shown in Figure 2, it is found that a plurality of openings 20 are formed in an electrode for electrolysis 10.

[0032] With respect to the above (I), the opening ratio (%) can be calculated in accordance with the following formula:

$$100 \times (w1-w2)/w1$$

wherein w1 represents the weight of a paper sheet before openings are cut out; and w2 represents the weight of the paper sheet after all openings are cut out. The sum of perimeters can be obtained by adding up the perimeters of opening images cut out.

[0033] With respect to the above (II), image data are analyzed by the image processing method, for example, "Image J", developed and open to public by the US National Institutes Of Health (NIH).

[0034] If value C (= B/A), which is obtained by dividing sum B of perimeters of openings of an electrode for electrolysis by opening ratio A of the electrode for electrolysis, is 2 or less, the electrode for electrolysis has a large opening ratio or a few number of large openings. In this case, since the specific surface area of the electrode for electrolysis decreases, an apparent current density increases and electrolysis voltage increases. If value C is beyond 5, a conductive substrate has a small opening ratio; in other words, a large number of small openings, which adversely affects circulation of an electrolyte solution and desorption of gas generated at an electrode and may result in increasing an electrolysis voltage.

[0035] In the prior art, various techniques for reducing electrolysis voltage are disclosed on the basis that the thickness of an electrode is 0.5 mm or less. However, in the first electrode for electrolysis, the thickness of the electrode for electrolysis is specified as more than 0.5 mm and 1.2 mm or less and value C (= B/A), which is obtained by dividing sum B of perimeters of openings of the electrode for electrolysis by opening ratio A, is specified as more than 2 and 5 or less. In this way, an electrode for electrolysis not only keeping down voltage and power consumption during electrolysis but also having practical strength is obtained.

[0036] In the electrode for electrolysis according to the present embodiment, the opening ratio of the electrode for electrolysis is preferably 5% or more and less than 25%, more preferably 7% or more and 20% or less and particularly preferably 10% or more and 18% or less. If the opening ratio of the electrode for electrolysis is 5% or more, an adverse effect such as retention of gas generated at an electrode during electrolysis, tends to be successfully and effectively overcome without adversely affecting circulation of an electrolyte solution; and electrolysis voltage tends to be successfully reduced. In contrast, if the opening ratio of the electrode for electrolysis is less than 25%, the specific surface area of the electrode for electrolysis can be sufficiently obtained; in other words, substantial electrode surface facing an ion exchange membrane tends to be successfully sufficiently obtained, with the result that an apparent current density can be reduced and electrolysis voltage tends to be successfully reduced.

[0037] In the electrode for electrolysis according to the present embodiment, the perimeter of a single opening of the electrode for electrolysis is preferably 1 mm or more and more preferably, 2.5 mm or more. If the perimeter of a single opening of the electrode for electrolysis is 1 mm or more, pressure drop of electrolyte-solution flow in the opening can be kept down and electrolysis voltage tends to be successfully reduced. The perimeter of a single opening of the electrode for electrolysis is preferably 4.8 mm or less and more preferably 4.55 mm or less in order to sufficiently keep the specific surface area of the electrode for electrolysis. The perimeter of a single opening of the electrode for electrolysis can be measured by observing either one of the surfaces of the electrode for electrolysis by an image observation apparatus such as a microscope, photographing a projection plane and analyzing the image data (image analysis method).

[0038] In the electrode for electrolysis according to the present embodiment, it is preferable that the short width SW, which is the center-to-center distance of openings in the minor-axis direction of the mesh of the electrode for electrolysis, is 1.5 mm or more and 3 mm or less; whereas the long width LW, which is the center-to-center distance of openings in the major-axis direction of the mesh, is 2.5 mm or more and 5 mm or less. It is more preferable that the short width SW is 1.5 mm or more and 2.5 mm or less, whereas the long width LW is 3 mm or more and 4.5 mm or less.

[0039] SW and LW can be defined as shown in Figure 3. More specifically, SW can be specified as the distance between the centers of two adjacent openings in the minor-axis direction of a mesh. In contrast, LW can be specified as the distance between the centers of two adjacent openings in the major-axis direction of the mesh.

[0040] If SW is 1.5 mm or more and LW is 2.5 mm or more in the present embodiment, a suitable thickness and opening ratio can be easily obtained. If SW is 3 mm or less and LW is 5 mm or less in the present embodiment, a suitable range of opening ratio can be easily obtained; in other words, the specific surface area of the electrode for electrolysis can be easily obtained.

[0041] It is preferable that the distance d between openings shown in Figure 3 is controlled. Distance d is calculated as a square root of a value, which is obtained by adding a square of SW to a square of LW. As the value d decreases, mass transfer of a substance such as a gas tends to be more accelerated. From this point of view, a value d is preferably 2.9 to 5.8 mm and more preferably 3.4 to 5.1 mm.

[0042] In the electrode for electrolysis according to the present embodiment, value E, which is a value obtained from sum B of perimeters of openings, opening ratio A, short width SW and long width LW of the openings, and represented by the following formula (1), is preferably 0.5 or more, more preferably 0.69 or more and further preferably 0.69 or more and 1.5 or less.

$$E = B/(A \times (SW^2 + LW^2)^{1/2}) \qquad (1)$$

[0043] In formula (1), $(SW^2 + LW^2)^{1/2}$ corresponds to value d. As mentioned above, if the relationship among values A, B and d is controlled to fall within an appropriate range, the degree of spatial distribution of openings becomes suitable and electrolysis voltage tends to be successfully decreased. More specifically, if value E is 0.5 or more and 1.5 or less in an electrode for electrolysis, the degree of spatial distribution of openings of the electrode for electrolysis becomes suitable for circulation of an electrolyte solution and electrolysis voltage tends to be successfully decreased.

[0044] Then, the second electrode for electrolysis will be more specifically described. The second electrode for electrolysis is an electrode for electrolysis having a conductive substrate formed of a porous metal plate and at least one catalyst layer formed on a surface of the conductive substrate, in which the shape of openings is right-and-left symmetric about a first imaginary center line extending in the minor-axis direction of a mesh and up-and-down asymmetric about a second imaginary center line extending in the major-axis direction of the mesh; and the electrode for electrolysis has a thickness of more than 0.5 mm and 1.2 mm or less.

[0045] A typical example of an opening shape in the second electrode for electrolysis is shown in Figure 4 (A). In Figure 4 (A), an opening 100 is right-and-left symmetric about a first imaginary center line 101 extending in minor-axis direction α of the mesh. The right-and-left symmetry means that when an opening is partitioned in a right part and a left part with respect to the first imaginary center line, the shape of the right part matches up with the shape of the left part; more specifically, the right part and the left part are line symmetric with respect to the first imaginary center line. The right-and-left symmetry can be confirmed by the aforementioned image analysis.

[0046] The opening 100 is up-and-down asymmetric about a second imaginary center line 102 extending in major-axis direction β of the mesh. The up-and-down asymmetry means that when an opening is partitioned in an upper part and a lower part with respect to the second imaginary center line, the shape of the upper part fails to match up with the shape of the lower part; in other words, the shapes of the upper part and the lower part are not line symmetric with respect to the second imaginary center line. The right-and-left symmetry can be confirmed by the aforementioned image analysis. For example, in the example shown in Figure 4 (B), the opening 100 can be partitioned in upper portion a and lower portion b with respect to second imaginary center line 102 extending in major-axis direction β and up-and-down asymmetry can be easily confirmed by comparing the shapes of portion a and portion b.

[0047] Although the reason why the second electrode for electrolysis can keep low voltage and power consumption during electrolysis is not known, the present inventors presume as set forth below. In this context, the concept of the second electrode for electrolysis is not limited by the following presumption and as long as an electrode has the aforementioned constitution, the electrode can be included in the second electrode for electrolysis.

[0048] A typical shape of openings of a conventional electrode for electrolysis is right-and-left symmetric about the first imaginary center line and up-and-down symmetric about the second imaginary center line. For example, as shown in Figure 4 (C), an opening 100' is right-and-left symmetric about a first imaginary center line 101 extending in minor-axis direction α of a mesh. The opening 100' is, with respect to the upper portion a and lower portion b, line symmetric about a second imaginary center line 102 extending in major-axis direction β of the mesh. In this case, the shape of the opening is typically rhombus. The four sides constituting the opening are positioned in almost the same distance from the center point of the opening. In such a conventional electrode for electrolysis, when a gas generates and passes through the opening (typically spherical), the gas comes in contract with the four sides (more specifically, 4 points) constituting the opening, with the result that the airflow resistance presumably tends to increase. More specifically, the gas generated at an electrode during electrolysis tends to remain in contact with the interior of openings and adversely affects circulation of an electrolyte solution, with the result that an undesired increase of electrolysis voltage occurs.

[0049] In contrast, the second electrode for electrolysis is right-and-left symmetric about the first imaginary center line and up-and-down asymmetric about the second imaginary center line. Owing to the structure, the airflow resistance when a gas is generated at an electrode and passes through the opening (typically spherical) presumably tends to decrease. More specifically, since the number of contact points between a gas generated at an electrode during electrolysis and individual sides of the opening tends to reduce, the gas tends to be successfully desorbed, with the result that electrolysis voltage can be reduced without adversely affecting circulation of an electrolyte solution.

[0050] In the second electrode for electrolysis, the area of openings per projected area (1 cm^2) in either one of the surfaces, which is not particularly limited, is preferably 0.05 cm^2 or more in order to further reduce the voltage and power consumption during electrolysis. The number of openings per projected area (1 cm^2), which is not particularly limited, is preferably 15 or more in order to further reduce the voltage and power consumption during electrolysis. The area and number of openings can be determined by the aforementioned image analysis.

[0051] In the second electrode for electrolysis, when an opening is partitioned in portion a and portion b by the second imaginary center line, the value (Sa/Sb), which is obtained by dividing area Sa of the portion a by area Sb of the portion b, is preferably 1.15 or more and 2.0 or less. In this case, up-and-down asymmetry of the opening portion tends to become more apparent. More specifically, up-and-down asymmetry of the shape of an opening of an electrode for electrolysis about the second imaginary center line extending in the major-axis direction of the mesh is also suggested by the value of Sa/Sb. If the Sa/Sb value is 1.15 or more and 2.0 or less, gas generated at an electrode during electrolysis tends to be successfully and effectively desorbed without adversely affecting circulation of an electrolyte solution and electrolysis voltage tends to be successfully decreased. Sa and Sb correspond to the area of portion a and the area of portion b, respectively, in the example shown in Figure 4 (B) where a relationship Sa > Sb is satisfied. The values of Sa and Sb can be determined by the aforementioned image analysis.

[0052] In the second electrode for electrolysis, a value (St/SW), which is obtained by dividing St, which is a value obtained by subtracting an maximum size of openings in the minor axis direction of a mesh from center-to-center distance SW of openings in the minor-axis of the mesh, by SW, is preferably 0.4 or more and more preferably more than 0.67 and less than 1.0. In the example shown in Figure 5, a plurality of openings are formed in an electrode for electrolysis 300. SW is specified by a center-to-center distance 310 of the adjacent two openings in the minor-axis direction of a mesh. The "adjacent two openings" herein means first opening and second opening, with which a first imaginary center line extended from the first opening first comes in contact. LW is specified by a center-to-center distance 320 of the adjacent two openings in the major-axis direction of the mesh. The "adjacent two openings" herein means first opening and second opening, with which a second imaginary center line extended from the first opening first comes in contact. Note that, in Figure 5, a second imaginary center line 330 partitions an opening in portion a and portion b in the electrode for electrolysis 300. It is found that portion a (340) and portion b (350) are up-and-down asymmetry about the imaginary center line 330. In Figure 5, the distance 360 between adjacent two openings in the minor-axis direction of the mesh correspond to value St, which is obtained by subtracting a maximum size of openings in the minor-axis direction of the mesh from center-to-center distance SW of the openings in the minor-axis direction of the mesh. Note that, the maximum size of an opening in the minor-axis direction of the mesh in the example shown in Figure 4 (A) corresponds to the length of the first imaginary center line 101. If St/SW is 0.4 or more, the specific surface area of the electrode for electrolysis can be sufficiently obtained without adversely affecting circulation of an electrolyte solution, and electrolysis voltage tends to be successfully decreased. Values St and SW can be determined by the aforementioned image analysis.

[0053] The electrode for electrolysis according to the present embodiment is constituted by forming at least one catalyst layer on a surface of the aforementioned conductive substrate. In order to improve adhesion to the catalyst layer, the surface of the conductive substrate in contact with the catalyst layer is preferably subjected to a treatment for increasing a surface area of the conductive substrate. Examples of the treatment for increasing a surface area include, but are not limited to, a blast treatment using cut wire, steel grid and alumina grid; and an acid treatment using sulfuric acid or hydrochloric acid. Of these treatments, a blast treatment for roughening the surface of a conductive substrate, followed by an acid treatment, is preferable.

(Catalyst layer)

[0054] In the electrode for electrolysis according to the present embodiment, the catalyst layer to be formed on the surface of a conductive substrate, preferably on the surface of a conductive substrate to which the aforementioned treatment is previously applied, preferably contains an electrocatalytic substance such as an oxide of a platinum group metal, magnetite, ferrite, cobalt spinel, or a metal oxide mixture in order to reduce electrolysis voltage. Of the electrocatalytic substances mentioned above, a ruthenium element, an iridium element and a titanium element are preferable and they are more preferably present in the form of an oxide in order to keep low voltage during electrolysis.

[0055] Examples of the ruthenium oxide include, but are not limited to, RuO_2.

[0056] Examples of the iridium oxide include, but are not limited to, IrO_2.

[0057] Examples of the titanium oxide include, but are not limited to, TiO_2.

[0058] In the catalyst layer of the electrode for electrolysis according to the present embodiment, ruthenium oxide, iridium oxide and titanium oxide preferably form a solid solution. If ruthenium oxide, iridium oxide and titanium oxide form a solid solution, durability of the ruthenium oxide is further improved and electrolysis voltage tends to be kept down for a long term.

[0059] The solid solution means that two types or more substances mutually dissolve to form an entirely homogenous solid phase. As the substances forming a solid solution, e.g., a single metal and a metal oxide are mentioned. Particularly in the case of a solid solution of a metal oxide suitable for the present embodiment, two types or more metal atoms are irregularly aligned on equivalent lattice points in a unit lattice of an oxide crystal structure. More specifically, it is preferable that a ruthenium oxide, an iridium oxide and a titanium oxide are mutually mixed to form a substitutional solid solution in which a ruthenium atom is replaced with an iridium atom or a titanium atom or both of them, as viewed from the ruthenium oxide's side. The state of the solid solution is not particularly limited and a region having a partial solid solution may present.

[0060] The size of a unit lattice of a crystal structure is slightly changed by a solid solution. The degree of the change can be determined, for example, by powder X ray diffraction based on a shift of a peak position derived from the size of a unit lattice without causing any change of a diffraction pattern derived from a crystal structure.

[0061] In the catalyst layer of the electrode for electrolysis according to the present embodiment, the content ratio of a ruthenium element, an iridium element and a titanium element by mole is preferably 1: 0.2 to 3: 0.2 to 8; more preferably 1: 0.3 to 2: 0.2 to 6; and particularly preferably 1: 0.5 to 1.5: 0.2 to 3. If the content ratio of the three elements falls within the above range, the long-term durability of the electrode for electrolysis tends to be more improved. Iridium, ruthenium and titanium may be contained in the catalyst layer in the form other than an oxide, for example, a single metal.

[0062] The catalyst layer in the electrode for electrolysis according to the present embodiment may contain only a ruthenium element, an iridium element and a titanium element as constitutional elements or may contain metal elements other than these. Examples of the other metal elements include, but are not limited to, elements selected from, e.g., tantalum, niobium, tin, platinum and vanadium. These metal elements may be contained, for example, as metal elements of oxides.

[0063] In the present embodiment, if the catalyst layer contains other metal elements, the content ratio of the elements relative to the total metal elements contained in the catalyst layer by mole is preferably 20 mol % or less and more preferably 10 mol % or less.

[0064] In the present embodiment, the thickness of the catalyst layer is preferably 0.1 to 5 μm and more preferably 0.5 to 3 μm. If the thickness of the catalyst layer is the lower limit (mentioned above) or more, initial electrolysis performance tends to be successfully and sufficiently maintained. If the thickness of the catalyst layer is the upper limit (mentioned above) or less, economical and excellent electrode for electrolysis tends to be obtained. The thickness of the catalyst layer can be determined by cutting the substrate and subjecting a section of the substrate to measurement under an optical microscope or an electronic microscope.

[0065] The catalyst layer may be constituted of a single layer or two or more layers. If the catalyst layer is constituted of two layers or more, it is satisfactory if at least one of the layers is the catalyst layer according to the present embodiment. If the catalyst layer is constituted of two layers or more, it is preferable that at least the innermost layer is the catalyst layer according to the present embodiment. If at least the innermost layer is a solid solution formed of a ruthenium oxide, an iridium oxide and a titanium oxide, durability of the catalyst layer tends to be further improved. The case in which the catalyst layer according to the present embodiment consists of two or more layers which is same or different in composition, is preferable.

[0066] Even in the case where the catalyst layer consists of two or more layers, the thickness of the catalyst layer according to the present embodiment is preferably 0.1 to 5 μm and more preferably 0.5 to 3 μm, as mentioned above.

(Method for producing electrode for electrolysis)

[0067] A method for producing the electrode for electrolysis according to the present embodiment will be described by taking a case where an expanded metal is used as the conductive substrate, as an example.

[0068] The electrode for electrolysis according to the present embodiment can be produced by forming an expanded metal as a conductive substrate by expanding a flat plate made of a valve metal while slitting up by an upper blade and a lower blade to form a mesh, and flattening the mesh up to a desired thickness by applying pressure by e.g., a mill roll; applying the surface area increasing treatment mentioned above to the conductive substrate; and thereafter, forming a catalyst layer containing a ruthenium element, an iridium element and a titanium element on the conductive substrate.

[0069] The method for producing an expanded metal according to the present embodiment has a step of forming a mesh by extending a flat plate made of a valve metal while slitting up by an upper blade and a lower blade and a step of flattening the mesh by applying pressure by e.g., a mill roll. Owing to these steps, the expanded metal, satisfying the thickness of the resultant electrode for electrolysis (which is formed by providing at least one catalyst layer on a surface of the conductive substrate) of more than 0.5 mm and 1.2 mm or less and satisfying value C (= B/A), (which is obtained by dividing sum B of perimeters of openings of the electrode for electrolysis by opening ratio A of the electrode for electrolysis) of more than 2 and 5 or less, can be produced.

[0070] The thickness of the electrode for electrolysis can be controlled to fall within a suitable range of the present embodiment by controlling the thickness of the flat plate made of a valve metal to be used as a material for a conductive substrate and controlling rolling strength at the time of flattening the mesh by applying pressure by e.g., a mill roll.

[0071] The opening ratio of the electrode for electrolysis and center-to-center distance SW of openings in a minor-axis direction of the mesh can be controlled to fall within suitable ranges of the present embodiment, by controlling the step size of a feed roller, which moves in conjunction with up-and-down movement of the upper blade to continuously feed the plate forward, in a step of forming a mesh by extending a flat plate made of a valve metal while slitting up by an upper blade and a lower blade. More specifically, in order to control the degree of variance of openings of the present embodiment, the step size at the time of forming slits in the flat plate made of a valve metal by an upper blade and a lower blade is preferably controlled to be 0.8 mm or less. In order to maintain the shape of openings of the present embodiment, the step size is preferably 0.5 mm or more.

[0072] Center-to-center distance LW of openings in a major-axis direction of the mesh can be controlled to fall within a suitable range of the present embodiment by appropriately selecting the shapes of the upper blade and the lower blade used for forming a slit in a flat plate made of a valve metal.

[0073] The sum of perimeters of openings of the electrode for electrolysis, which increases or decreases depending on the increase or decrease of the number of openings, can be controlled by, e.g., the number of upper blades and lower blades.

[0074] In contrast, a porous plate such as a perforated metal, which is employed as a conductive substrate, can be obtained by making holes in a metal flat plate by use of a mold of a punching press. At this time, if, for example, shape and arrangement of the mold, are appropriately chosen, the opening ratio, the sum of perimeters of openings, SW and LW can be controlled to fall within suitable ranges of the present embodiment.

[0075] A metallic mesh, if it is employed as the conductive substrate, can be obtained by weaving a plurality of metal wires (for forming a metallic mesh) which are obtained by various methods known in the art. At this time, if, for example, the weight (corresponding to denier or thickness of metal wire) of the metal wire (for forming a metallic mesh) per unit length and the number of metal wires (mesh number) to be woven per unit area of the metallic mesh are appropriately selected, the opening ratio, the sum of perimeters of openings, SW and LW can be controlled to fall within suitable ranges of the present embodiment. If control is made in the same manner as above, the shape of the second electrode for electrolysis tends to be easily obtained.

[0076] A catalyst layer is formed on the conductive substrate preferably by a thermal decomposition technique.

[0077] In a production method using the thermal decomposition technique, a catalyst layer can be formed by applying a coating liquid containing a mixture of compounds (precursors) containing the aforementioned elements; and calcination under an atmosphere containing oxygen to thermally decompose the components in the coating liquid. According to this method, the electrode for electrolysis can be produced with a high productivity in fewer steps than in conventional production method.

[0078] The thermal decomposition herein means that, e.g., a metal salt as a precursor is calcined under an atmosphere containing oxygen to decompose the metal salt into a metal oxide or a metal and a gaseous substance. The decomposition product to be obtained can be controlled depending on the types of metal, types of metal salts contained in the precursors to be blended in the coating liquid and the atmosphere for thermal decomposition. Usually, under an oxidizing atmosphere, a number of metals tend to be easily formed into oxides. In industrial production process for an electrode for electrolysis, thermal decomposition is usually carried out in the air. Also, in the present embodiment, the range of oxygen concentration during calcination is not particularly limited and thermal decomposition is sufficiently carried out in the air. However, if necessary, air or oxygen may be supplied in the calcination furnace.

[0079] The compounds to be contained in the coating liquid such as a ruthenium compound, an iridium compound and a titanium compound may be oxides; however, they are not necessarily oxides and may be, for example, metal salts. As the metal salt, which is not limited to, any one selected from the group consisting of a chloride, nitrate, sulfate and a metal alkoxide is mentioned.

[0080] Examples of a metal salt of the ruthenium compound include, but are not limited to, ruthenium chloride and ruthenium nitrate.

[0081] Examples of a metal salt of the iridium compound include, but are not limited to, iridium chloride and iridium nitrate.

[0082] Examples of a metal salt of the titanium compound include, but are not limited to, titanium tetrachloride.

[0083] The compounds mentioned above are appropriately selected depending on a desired metal element ratio in the catalyst layer and put in use.

[0084] The coating liquid may further contain compounds other than the aforementioned compounds. Examples of the other compounds include, but are not limited to, metal compounds containing a metal element such as tantalum, niobium, tin, platinum, rhodium, vanadium; and organic compounds containing a metal element such as tantalum, niobium, tin, platinum, rhodium and vanadium.

[0085] The coating liquid is preferably a liquid composition prepared by dissolving or dispersing the aforementioned compounds in an appropriate solvent. The solvent to be used in the coating liquid here can be selected depending on the types of compounds. For example, water; and an alcohol such as butanol, can be used. The total concentration of compounds in the coating liquid, which is not particularly limited, is preferably 10 to 150 g/L in order to properly control the thickness of the catalyst layer.

[0086] Examples of a method for applying the coating liquid onto a surface of the conductive substrate, include, but are not limited to, a dip method in which a conductive substrate is dipped in a coating liquid, a method of applying a coating liquid to a surface of a conductive substrate with a brush, a roll method in which a conductive substrate is allowed to pass between sponge-like rolls impregnated with a coating liquid and an electrostatic application method in which a conductive substrate and a coating liquid are oppositely charged and the coating liquid is sprayed. Of these coating methods, the roll method and electrostatic coating method are preferable since they are excellent in industrial productivity. Using either one of these coating methods, a coating film of a coating liquid can be formed on at least one of the surfaces of the conductive substrate.

[0087] After the conductive substrate is coated with a coating liquid, if necessary, a step of drying the coating film is preferably carried out. Owing to the drying step, the coating film can be more strongly formed on a surface of the conductive substrate. The drying conditions can be appropriately selected depending on, e.g., the composition and type of solvent of the coating liquid. The drying step is preferably carried out at a temperature of 10 to 90°C for 1 to 20 minutes.

[0088] After a coating film of a coating liquid is formed on a surface of the conductive substrate, the film is calcined under an atmosphere containing oxygen. The calcination temperature can be appropriately selected depending on the composition and type of solvent of the coating liquid. The calcination temperature is preferably 300 to 650°C. If the calcination temperature is less than 300°C, a decomposition of a precursor of e.g., a ruthenium compound becomes insufficient, with the result that a catalyst layer containing e.g., a ruthenium oxide cannot be obtained. If the calcination temperature exceeds 650°C, a conductive substrate may be oxidized in some cases, with the result that adhesion between the catalyst layer and the substrate may decrease. Particularly, if a substrate made of titanium is used as the conductive substrate, it should be important to consider this tendency.

[0089] The calcination time is preferably long; however, in view of productivity of an electrode, calcination time is preferably controlled so as not to be excessively long. In consideration of these, a single calcination time is preferably 5 to 60 minutes.

[0090] If necessary, the aforementioned steps of coating, drying and calcination of a catalyst layer are repeated several times to form the catalyst layer having a desired thickness. After the catalyst layer is formed, calcination is carried out for a further long time as necessary. If so, stability of the catalyst layer chemically, physically and thermally extremely stable, can be further improved. As the conditions for long-time calcination, calcination at 400 to 650°C for about 30 minutes to 4 hours, is preferable.

[0091] If the electrode for electrolysis according to the present embodiment is used, overvoltage is low even in the initial stage of electrolysis, and electrolysis can be carried out at a low overvoltage and a low power consumption for a long term. Because of this, the electrode for electrolysis can be used in various types of electrolysis processes. Particularly, the electrode for electrolysis can be preferably used as an anode for chlorine generation and more preferably as anode for sodium chloride electrolysis by ion exchange membrane process.

(Electrolyzer)

[0092] The electrolyzer of the present embodiment has the electrode for electrolysis according to the present embodiment. More specifically, the electrolyzer of the present embodiment has an anode chamber containing the electrode for electrolysis according to the present embodiment as an anode and a cathode chamber containing a cathode and an ion exchange membrane isolating the anode chamber from the cathode chamber. Electrolysis is carried out at low initial voltage in the electrolyzer. A sectional view of the electrolyzer of the present embodiment is schematically shown in

Figure 6.

[0093] An electrolyzer 200 has an electrolyte solution 210, a container 220 for storing the electrolyte solution 210, an anode 230 and a cathode 240 dipped in the electrolyte solution 210, an ion exchange membrane 250 and wirings 260 for connecting the anode 230 and the cathode 240 to a power supply. Of the spaces of the electrolyzer 200 created by partition of the ion exchange membrane 250, the space on the side of the anode is referred to as an anode chamber and the space on the side of the cathode is referred to as a cathode chamber. The electrolyzer of the present embodiment can be used for various electrolysis processes. In the following, the case where the electrolyzer is used for an aqueous alkali chloride solution will be described as the typical example.

[0094] As the electrolyte solution 210 to be supplied to the electrolyzer of the present embodiment, for example, an aqueous alkali chloride solution having 2.5 to 5.5N, such as an aqueous sodium chloride solution (brine) and an aqueous potassium chloride solution, can be used in the anode chamber; whereas, a diluted aqueous alkaline hydroxide solution (for example, aqueous sodium hydroxide solution, aqueous potassium hydroxide solution) or water, can be used in the cathode chamber.

[0095] As the anode 230, the electrode for electrolysis according to the present embodiment is used.

[0096] As the ion exchange membrane 250, for example, a fluororesin film having an ion exchange group can be used. Of the ion exchange membranes, an ion exchange membrane having projections (micro-projections: delta shape), which are formed of the same polymer as used in forming the ion exchange membrane, on the surface facing the anode, is preferably used in combination with the electrode for electrolysis according to the present embodiment in the electrolyzer. As an example of the electrolyzer, for example "Aciplex" (registered trade mark) F6801 (manufactured by Asahi Kasei Corporation) can be mentioned.

[0097] If the ion exchange membrane having a delta shape is used, brine supply to a space between the ion exchange membrane and the anode is accelerated, damage of the ion exchange membrane and an increase of the concentration of salt in caustic soda tend to be suppressed. If the ion exchange membrane having a delta shape and the electrode for electrolysis according to the present embodiment are used in combination, stable electrolysis performance can be maintained. As a method for forming projections, which is not particularly limited, for example, methods described in Japanese Patent No. 4573715 and Japanese Patent No. 4708133, can be used.

[0098] As the cathode 240, e.g., a cathode for hydrogen generation, which is an electrode formed by applying a catalyst onto a conductive substrate, is used. As the cathode, a cathode known in the art can be employed. Examples thereof include a cathode formed by applying nickel, nickel oxide, a nickel-tin alloy, a combination of activated carbon and an oxide, ruthenium oxide or platinum onto a nickel base; and a cathode formed by coating a metallic-mesh substrate made of nickel with ruthenium oxide.

[0099] The structure of the electrolyzer of the present embodiment, which is not particularly limited, may be a single pole type or a bipolar type. Materials for constituting the electrolyzer are not particularly limited. For example, as a material for the anode chamber, e.g., titanium resistant to an alkali chloride and chlorine, is preferable. As a material for a cathode chamber, e.g., nickel resistant to an alkali hydroxide and hydrogen, is preferable.

[0100] The electrode (the anode 230) for electrolysis according to the present embodiment may be arranged at an appropriate interval with the ion exchange membrane 250 or in contact with ion exchange membrane 250. Both cases, the electrolyzer be used without any problem. The cathode 240 may be arranged at an appropriate interval with ion exchange membrane 250. The electrolyzer may be a zero-gap base electrolyzer having no interval with the ion exchange membrane 250. Both cases, the electrode can be used without any problem.

[0101] As the electrolytic conditions of the electrolyzer of the present embodiment, which are not particularly limited, known conditions can be employed. For example, electrolysis can be carried out preferably at a temperature of 50 to 120°C and a current density of 0.5 to 10 kA/m^2.

(Reactivation of electrode for electrolysis)

[0102] The electrode for electrolysis according to the present embodiment can be suitably used for renewing an existing catalyst-coated electrode used in an electrolyzer when the activity of the electrode decreased. More specifically, a method for renewing an electrode in the present embodiment include a step of welding the electrode for electrolysis according to the present embodiment on the existing electrode in an electrolyzer. Likewise, just by newly welding the electrode for electrolysis according to the present embodiment on an existing electrode, electrolysis performance of the existing electrode decreased in activity can be returned to the level before deterioration or further improved; in other words, the electrode can be easily reactivated. In conventional methods, an existing electrode decreased in activity is renewed by two steps: a step of removing the existing electrode from the electrolyzer and a step of further welding a new electrode. Such load during a renewing process for the electrode can be reduced.

[0103] The electrode for electrolysis according to the present embodiment attached by welding and the existing electrode present in the electrolyzer can be regarded as a laminate. More specifically, the electrode laminate of the present embodiment has the electrode for electrolysis according to the present embodiment and a base electrode for electrolysis different from the aforementioned electrode for electrolysis. The base electrode herein, which is not particularly limited, is typically an existing electrode present in an electrolyzer as mentioned above and decreased in activity.

[0104] Note that, the electrode for electrolysis according to the present embodiment suitable for reactivation of the electrode for electrolysis preferably has a thickness of more than 0.5 mm and 0.65 mm or less, and value C (= B/A) (which is obtained by dividing sum B of perimeters of openings of the electrode for electrolysis by opening ratio A) of more than 2 and 5 or less. If the thickness falls within the aforementioned range, it is easy to weld a new electrode on an existing electrode and electrolysis performance can be returned to the level before deterioration without particularly changing the internal structure, parts and etc., used in the existing electrolyzer, or can be further improved; in other words, the electrode can be reactivated. More specifically, in the electrode laminate of the present embodiment, the thickness of the electrode for electrolysis is preferably more than 0.5 mm and 0.65 mm or less.

[0105] The electrode for electrolysis according to the present embodiment can reduce the electrolysis voltage during brine electrolysis more than conventional electrodes. Because of this, according to the electrolyzer of the present embodiment having the electrode for electrolysis, it is possible to reduce power consumption required for brine electrolysis.

[0106] Since the electrode for electrolysis according to the present embodiment has a catalyst layer chemically, physically and thermally extremely stable, the electrode is excellent in long-term durability. Thus, according to the electrolyzer of the present embodiment having the electrode for electrolysis, catalytic activity of the electrode can be maintained high for a long time and highly pure chlorine can be stably produced.

Examples

[0107] Hereinafter, the present embodiment will be more specifically described based on Examples; however, the present embodiment is not limited to these Examples alone.

[0108] First of all, evaluation methods used in Examples and Comparative Examples will be described below.

(Experiment of sodium chloride electrolysis by ion exchange membrane process)

[0109] As an electrolytic cell, an electrolytic cell having an anode cell having an anode chamber and a cathode cell having a cathode chamber was prepared.

[0110] Electrodes for electrolysis prepared in individual Examples and Comparative Examples were cut into pieces having a predetermined size (95×110 mm = 0.01045 m^2) and used as test electrodes. Each of the test electrodes was attached to a rib of an anode chamber of an anode cell by welding and used as an anode.

[0111] As a cathode, an electrode prepared by coating a metallic mesh substrate made of nickel with ruthenium oxide as a catalyst, was used. In the first place, an expanded substrate made of a nickel metal and serving as a collector was cut into pieces having the same size as in the anode and attached by welding on the rib of the cathode chamber of the cathode cell, and thereafter, a cushion mat woven of nickel wire was placed and a cathode was placed on the cushion.

[0112] As a gasket, a rubber gasket made of EPDM (ethylene propylene diene) was used for sandwiching an ion exchange membrane between the anode cell and the cathode cell. As the ion exchange membrane, cation exchange membrane "Aciplex" (registered trade mark) F6801 (manufactured by Asahi Kasei Corporation) for brine electrolysis was used.

[0113] Electrolysis voltage was determined by measuring the potential difference between the cathode and the anode. To determine the initial electrolysis performance of the anode, electrolysis voltage of Day 5 after initiation of electrolysis was measured. Electrolysis was carried out in the conditions: current density: 6 kA/m^2, brine concentration in the anode cell: 205 g/L, NaOH concentration in the cathode cell: 32 mass% and temperature: 90°C. As a rectifier for electrolysis, "PAD36-100LA" (manufactured by Kikusui Electronics Corporation) was used.

[Example 1]

[0114] As a conductive substrate, an expanded metal made of titanium and having a center-to-center distance (SW) in the minor-axis direction of a mesh of 2.1 mm, a center-to-center distance (LW) in the major-axis direction of the mesh of 3 mm and a plate-thickness of 0.81 mm, was used. The plate-thickness was measured by a thickness gauge. The values of SW, LW, St, opening ratio and the sum of perimeters of openings were determined by observing a specified range of the surface of the conductive substrate by an image observation apparatus such as e.g., a microscope, photographing a projection plane and analyzing image data. As a method for analyzing image data, for example, "Image J" developed by the US National Institutes Of Health (NIH) and open to public, was used for processing images. The size of the image of the conductive substrate subjected to image processing falls within the range of 8.0×5.3 mm. More specifically, an openings present within the range were used as targets. The center-to-center distance in the minor-axis direction of a mesh specified between each pair of adjacent openings, the center-to-center distance in the major-axis direction of the mesh and a value, which is obtained by subtracting a maximum opening size of openings in the minor-axis direction of a mesh from the center-to-center distance of openings in the minor-axis direction of the mesh were measured, averaged and regarded as SW, LW and St, respectively. With respect to the conductive substrate and electrode for electrolysis in each of Examples and Comparative Examples, SW, LW, St, opening ratio A, sum B of perimeters of openings, the perimeter of a single opening, E (= $B/(A \times (SW^2 + LW^2)^{1/2})$) and thickness value were obtained in the same manner as in the above. The expanded metal was calcined in the air at 540°C for 4 hours to form an oxide film on the surface, and thereafter, treated with a 25 wt% sulfuric acid solution at 85°C for 4 hours. In this manner, a pretreatment for roughening the surface of the conductive substrate was applied.

[0115] Subsequently, titanium tetrachloride (manufactured by Kishida Chemical Co., Ltd.) was added drop by drop to an aqueous ruthenium chloride solution (ruthenium concentration 100 g/L, manufactured by Tanaka Kikinzoku Co., Ltd.) while cooling the solution by dry ice up to 5°C or less and stirring, such that the elemental ratio (molar ratio) of ruthenium, iridium and titanium becomes 25: 25: 50, and thereafter an aqueous iridium chloride solution (iridium concentration 100 g/L, manufactured by Tanaka Kikinzoku Co., Ltd.) was added drop by drop, to obtain an aqueous solution having a total metal concentration of 100 g/L, i.e., coating liquid CL1. On the other hand, the aqueous ruthenium chloride solution and titanium tetrachloride were mixed in the same manner as above, such that the elemental ratio (molar ratio) of ruthenium and titanium becomes 35: 65, to obtain an aqueous solution having a total metal concentration of 100 g/L, i.e., coating liquid CL2.

[0116] Coating liquid CL1 was poured in a fluid-receiving tray of a coating machine and an EPDM sponge roll was dipped and allowed to absorb the liquid while rotating the roll. On the upper portion of the sponge roll, a roll made of PVC was placed so as to be in contact with the upper portion. Then, the conductive substrate pretreated was passed through between the EPDM sponge roll and the PVC roll to apply CL1 to the conductive substrate. Immediately after application of CL1, the coated conductive substrate was passed through between two EPDM sponge rolls surrounded by cloth. In this manner, excessive coating liquid was wiped off. Thereafter, the conductive substrate was dried at 50°C for 10 minutes and calcined in the air at 475°C for 10 minutes.

[0117] A cycle consisting of coating by roll, drying and calcination as mentioned above was repeated 7 times in total and then calcination at 520°C for one hour was further carried out to form a black-brown first catalyst layer on the conductive substrate. The substrate having the first catalyst layer formed thereon was subjected to coating by roll in the same manner as in the process using coating liquid CL1 except that the coating liquid was changed to CL2, and then, subjected to drying and calcination in the air at 440°C for 10 minutes. Finally, the substrate was calcined in the air at 440°C for 60 minutes to produce an electrode for electrolysis.

[0118] The resultant electrode for electrolysis had a thickness of 0.81 mm and an opening ratio of 7.4%. The number of openings in the projected area of the electrode was more than 20 openings/cm^2 and a value, which is obtained by dividing the sum of perimeters of openings by the opening ratio, was 4.54. The shape of the openings observed was the same as in Figure 4 (A). The opening 100 was right-and-left symmetric about the first imaginary center line 101 extending in minor-axis direction α of a mesh. The opening 100 was up-and-down asymmetric about the second imaginary center line extending 102 in major-axis direction β of the mesh. A value, which is obtained by dividing the area Sa of portion a by area Sb of portion b, was 1.28 and a value, which is obtained by dividing St by SW, was 0.76.

[Comparative Example 1]

[0119] An electrode for electrolysis was produced in the same manner as in Example 1 except that the conductive substrate of Example 1 was changed to an expanded metal made of titanium and having a thickness of 1.0 mm, in which the center-to-center distance (SW) in the minor-axis direction of a mesh was 3 mm and the center-to-center distance (LW) in the major-axis direction of the mesh was 6 mm.

[0120] The resultant electrode for electrolysis had a thickness of 1.0 mm and an opening ratio of 37.8%. The number of openings in the projected area of the electrode was 13 openings/cm^2 and a value, which is obtained by dividing the sum of perimeters of openings by the opening ratio, was 1.06. The shape of the openings observed was the same as in Figure 4 (C). The opening 100' was right-and-left symmetric about the first imaginary center line 101 extending in minor-axis direction α of a mesh. The opening 100' was up-and-down symmetric about the second imaginary center line extending 102 in major-axis direction β of the mesh. A value, which is obtained by dividing the area Sa of portion a by area Sb of portion b, was 1.03 and a value, which is obtained by dividing St by SW, was 0.667.

[Example 2]

[0121] An electrode for electrolysis was produced in the same manner as in Example 1 except that the conductive substrate of Example 1 was changed to an expanded metal made of titanium and having a thickness of 0.8 mm, in which the center-to-center distance (SW) in the minor-axis direction of a mesh was 2.2 mm and the center-to-center distance (LW) in the major-axis direction of the mesh was 4.2 mm.

[0122] The resultant electrode for electrolysis had a thickness of 0.80 mm and an opening ratio of 10.9%. The number of openings in the projected area of the electrode was 20 openings/cm^2 and a value, which is obtained by dividing the sum of perimeters of openings by the opening ratio, was 3.26. The shape of the openings observed was the same as in Figure 4 (A). The opening 100 was right-and-left symmetric about the first imaginary center line 101 extending in minor-axis direction α of a mesh. The opening 100 was up-and-down asymmetric about the second imaginary center line extending 102 extending in major-axis direction β of the mesh. A value, which is obtained by dividing the area Sa of portion a by area Sb of portion b, was 1.64 and a value, which is obtained by dividing St by SW, was 0.73.

[Example 3]

[0123] An electrode for electrolysis was produced in the same manner as in Example 1 except that the conductive substrate of Example 1 was changed to an expanded metal made of titanium and having a thickness of 0.83 mm, in which the center-to-center distance (SW) in the minor-axis direction of a mesh was 2.3 mm and the center-to-center distance (LW) in the major-axis direction of the mesh was 3.3 mm.

[0124] The resultant electrode for electrolysis had a thickness of 0.83 mm and an opening ratio of 9.25 %. The number of openings in the projected area of the electrode was more than 20 openings/cm^2 and a value, which is obtained by dividing the sum of perimeters of openings by the opening ratio, was 3.65. The shape of the openings observed was the same as in Figure 4 (A). The opening 100 was right-and-left symmetric about the first imaginary center line 101 extending in minor-axis direction α of a mesh. The opening 100 was up-and-down asymmetric about the second imaginary center line 102 extending in major-axis direction β of the mesh. A value, which is obtained by dividing the area Sa of portion a by area Sb of portion b, was 1.27 and a value, which is obtained by dividing St by SW, was 0.70.

[Example 4]

[0125] An electrode for electrolysis was produced in the same manner as in Example 1 except that the conductive substrate of Example 1 was changed to an expanded metal made of titanium and having a thickness of 0.81 mm, in which the center-to-center distance (SW) in the minor-axis direction of a mesh was 2.3 mm and the center-to-center distance (LW) in the major-axis direction of the mesh was 3.3 mm.

[0126] The resultant electrode for electrolysis had a thickness of 0.81 mm and an opening ratio of 22.1 %. The number of openings in the projected area of the electrode was more than 20 openings/cm^2 and a value, which is obtained by dividing the sum of perimeters of openings by the opening ratio, was 2.05. The shape of the openings observed was the same as in Figure 4 (A). The opening 100 was right-and-left symmetric about the first imaginary center line 101 extending in minor-axis direction α of a mesh. The opening 100 was up-and-down asymmetric about the second imaginary center line 102 extending in major-axis direction β of the mesh. A value, which is obtained by dividing the area Sa of portion a by area Sb of portion b, was 1.28 and a value, which is obtained by dividing St by SW, was 0.43.

[Example 5]

[0127] An electrode for electrolysis was produced in the same manner as in Example 1 except that the conductive substrate of Example 1 was changed to an expanded metal made of titanium and having a thickness of 0.56 mm, in which the center-to-center distance (SW) in the minor-axis direction of a mesh was 1.6 mm and the center-to-center distance (LW) in the major-axis direction of the mesh was 3.0 mm.

[0128] The resultant electrode for electrolysis had a thickness of 0.56 mm and an opening ratio of 17.5 %. The number of openings in the projected area of the electrode was more than 43 openings/cm^2 and a value, which is obtained by dividing the sum of perimeters of openings by the opening ratio, was 3.30. The shape of the openings observed was the same as in Figure 4 (A). The opening 100 was right-and-left symmetric about the first imaginary center line 101 extending in minor-axis direction α of a mesh. The opening 100 was up-and-down asymmetric about the second imaginary center line 102 extending in major-axis direction β of the mesh. A value, which is obtained by dividing the area Sa of portion a by area Sb of portion b, was 1.88 and a value, which is obtained by dividing St by SW, was 0.65.

[Example 6]

[0129] An electrode for electrolysis was produced in the same manner as in Example 1 except that the conductive substrate of Example 1 was changed to an expanded metal made of titanium and having a thickness of 0.81 mm, in which the center-to-center distance (SW) in the minor-axis direction of a mesh was 2.1 mm and the center-to-center distance (LW) in the major-axis direction of the mesh was 3.1 mm.

[0130] The resultant electrode for electrolysis had a thickness of 0.81 mm and an opening ratio of 15.5 %. The number of openings in the projected area of the electrode was more than 20 openings/cm^2 and a value, which is obtained by dividing the sum of perimeters of openings by the opening ratio, was 2.72. The shape of the openings observed was the same as in Figure 4 (A). The opening 100 was right-and-left symmetric about the first imaginary center line 101 extending in minor-axis direction α of a mesh. The opening 100 was up-and-down asymmetric about the second imaginary center line 102 extending in major-axis direction β of the mesh. A value, which is obtained by dividing the area Sa of portion a by area Sb of portion b, was 1.42 and a value, which is obtained by dividing St by SW, was 0.67.

[Example 7]

[0131] To the expanded metal made of titanium (SW: 2.2 mm, LW: 3.2 mm, thickness 0.82 mm) produced in the same manner as in Example 6, coating liquid CL1 of Example 1 was applied in the same manner as in Example 1 to form a first catalyst layer on the conductive substrate.

[0132] Subsequently, titanium tetrachloride (manufactured by Wako Pure Chemical Industries Ltd.) was added drop by drop to an aqueous ruthenium nitrate solution (ruthenium concentration 100 g/L, manufactured by Furuya Metal Co., Ltd.) while cooling by dry ice up to 5°C or less and stirring, and thereafter, an aqueous iridium chloride solution (iridium concentration 100 g/L, manufactured by Tanaka Kikinzoku Co., Ltd.) and vanadium chloride (III) (manufactured by Kishida Chemical Co., Ltd.) were added drop by drop, such that the elemental ratio (molar ratio) of ruthenium, iridium, titanium, and vanadium to 21.25: 21.25: 42.5: 15, to thereby obtain an aqueous solution having a total metal concentration of 100 g/L, i.e., coating liquid CL3. The substrate having the first catalyst layer formed thereon was subjected to one cycle consisting of roll coating using coating liquid CL3, drying and calcination in the same manner as in Example 1 except that the calcination temperature was set at 400°C. Then, the same cycle mentioned above was repeated three times with the exception that the calcination temperature was set at 450°C. Further, final calcination was carried out at 520°C for one hour. In this way, an electrode for electrolysis was produced.

[0133] The resultant electrode for electrolysis had a thickness of 0.82 mm and an opening ratio of 16.1%. The number of openings in the projected area of the electrode was more than 20 openings/cm^2 and a value, which is obtained by dividing the sum of perimeters of openings by the opening ratio, was 2.73. The shape of the openings observed was the same as in Figure 4 (A). The opening 100 was right-and-left symmetric about the first imaginary center line 101 extending in minor-axis direction α of a mesh. The opening 100 was up-and-down asymmetric about the second imaginary center line 102 extending in major-axis direction β of the mesh. A value, which is obtained by dividing the area Sa of portion a by area Sb of portion b, was 1.38 and a value, which is obtained by dividing St by SW, was 0.63.

[Comparative Example 2]

[0134] An electrode for electrolysis was produced in the same manner as in Example 1 except that the conductive substrate of Example 1 was changed to an expanded metal made of titanium and having a thickness of 0.6 mm and not flattened by a mill roll, in which the center-to-center distance (SW) in the minor-axis direction of a mesh was 2.3 mm and the center-to-center distance (LW) in the major-axis direction of the mesh was 3.0 mm.

[0135] The resultant electrode for electrolysis had a thickness of 0.6 mm and an opening ratio of 43.3%. A value, which is obtained by dividing the sum of perimeters of openings by the opening ratio, was 1.07. The shape of the openings observed was the same as in Figure 4 (C). The opening 100' was right-and-left symmetric about the first imaginary center line 101 extending in minor-axis direction α of a mesh. The opening 100' was up-and-down symmetric about the second imaginary center line 102 extending in major-axis direction β of the mesh. A value, which is obtained by dividing the area Sa of portion a by area Sb of portion b, was 0.90 and a value, which is obtained by dividing St by SW, was 0.45.

[Comparative Example 3]

[0136] An electrode for electrolysis was produced in the same manner as in Example 1 except that the conductive substrate of Example 1 was changed to an expanded metal made of titanium and having a thickness of 0.5 mm, in which the center-to-center distance (SW) in the minor-axis direction of a mesh was 2.1 mm and the center-to-center distance (LW) in the major-axis direction of the mesh was 4.0 mm.

[0137] The resultant electrode for electrolysis had a thickness of 0.5 mm and an opening ratio of 35.7%. A value, which is obtained by dividing the sum of perimeters of openings by the opening ratio, was 1.78. The shape of the openings observed was the same as in Figure 4 (C). The opening 100' was right-and-left symmetric about the first imaginary center line 101 extending in minor-axis direction α of a mesh. The opening 100' was up-and-down symmetric about the second imaginary center line 102 extending in major-axis direction β of the mesh. A value, which is obtained by dividing the area Sa of portion a by area Sb of portion b, was 1.10 and a value, which is obtained by dividing St by SW, was 0.48.

[Experiment of sodium chloride electrolysis by ion exchange membrane process]

[0138] Experiments of sodium chloride electrolysis by ion exchange membrane process were carried out by using the electrodes for electrolysis produced in Examples 1 to 6 and Comparative Examples 1 to 3. The results are shown in Table 1.

[0139] Note that in Table 1, a case where an expanded metal to be used as a conductive substrate was flattened by a mill roll was described as "FR ○", the case where flattening was not applied was described as "FR ×". The reduction amount of electrolysis voltage based on Comparative Example 1 was represented by a positive value in the column of "effect: ΔV".

[Table 1]

	FR	Thickness [mm]	SW [mm]	LW [mm]	A: Opening ratio [%]	Perimeter of single opening [mm]	B: Sum of perimeters [mm]	B/A	E	Effect: ΔV
Example 1	○	0.81	2.1	3.0	7.4	2.58	33.6	4.54	1.24	35
Example 2	○	0.80	2.2	4.2	10.9	4.49	35.5	3.26	0.69	43
Example 3	○	0.83	2.3	3.3	9.25	3.04	33.8	3.65	0.91	41
Example 4	○	0.81	2.3	3.3	22.1	4.52	45.2	2.05	0.51	8
Example 5	○	0.56	1.6	3.0	17.5	3.38	57.7	3.30	0.97	42
Example 6	○	0.81	2.1	3.1	15.5	3.52	42.1	2.72	0.73	19
Comparative Example 1	○	1.0	3.0	6.0	37.8	7.76	39.9	1.06	0.16	0
Comparative Example 2	×	0.60	2.3	3.0	43.3	4.88	46.4	1.07	0.28	-23
Comparative Example 3	○	0.50	2.1	4.0	35.7	5.13	63.7	1.78	0.39	-19

[0140] A reduction amount of electrolysis voltage at a current density of 6 kA/m^2 based on Comparative Example 1 was 35 mV in Example 1, 43 mV in Example 2, 41 mV in Example 3, 8 mV in Example 4, 42 mV in Example 5 and 19 mV in Example 6. It was found that all of them can reduce electrolysis voltage compared to Comparative Example 1.

[0141] In contrast, in Comparative Examples 2 and 3, electrolysis voltage increased by 23 mV and 19 mV, respectively, compared to Comparative Example 1.

[0142] Experiments of sodium chloride electrolysis by ion exchange membrane process were carried out by using the electrodes for electrolysis produced in Examples 6 to 7 and Comparative Example 1. The results are shown together with the type of coating liquid for catalyst layer in Table 2.

[Table 2]

	FR	Thickness [mm]	SW [mm]	LW [mm]	Coating liquid for first catalyst layer	Coating liquid for second catalyst layer	A: Opening ratio [%]	Perimeter of single opening [mm]	B: Sum of perimeters [mm]	B/A	E	Effect: ΔV
Comparative Example 1	○	1.0	3.0	6.0	CL1	CL2	37.8	7.76	39.9	1.06	0.16	0
Example 6	○	0.81	2.1	3.1	CL1	CL2	15.5	3.52	42.1	2.72	0.73	19
Example 7	○	0.82	2.2	3.2	CL1	CL3	16.1	3.48	44.0	2.73	0.70	39

[0143] A reduction amount of electrolysis voltage at a current density of 6 kA/m^2 based on Comparative Example 1 was 19 mV in Example 6 and 39 mV in Example 7. It was found that all of them can reduce electrolysis voltage compared to Comparative Example 1. In particular, from comparison between Example 6 and Example 7, it was found that if the electrode for electrolysis according to the present embodiment has a vanadium-containing catalyst layer, the reduction effect of electrolysis voltage further increases.

[Example 8]

[0144] The electrode for electrolysis of Example 5 was used for re-activating an electrode decreased in activity. As the electrode decreased in activity, an electrode for electrolysis produced in the same manner as in Comparative Example 1 and used in an electrolyzer of a semi-commercial plant for 6.9 years by supplying power, was used. The electrode was cut into pieces having a predetermined size (95 × 110 mm = 0.01045 m^2) and used as a base electrode. The base electrode was attached to the rib of an anode chamber of an anode cell by welding. The electrolysis voltage of the base electrode at a current density of 6 kA/m^2 increased by 32 mV based on that of Comparative Example 1.

[0145] To the base electrode, the electrode for electrolysis of Example 5 was attached by welding as a renewal electrode to produce an electrolyzer containing an electrode laminate.

[Example 9]

[0146] An electrode for electrolysis was produced in the same manner as in Example 1 except that the conductive substrate of Example 1 was changed to an expanded metal made of titanium and having a thickness of 0.52 mm in which the center-to-center distance (SW) in the minor-axis direction of a mesh was 2.2 mm and the center-to-center distance (LW) in the major-axis direction of the mesh was 3.0 mm.

[0147] The resultant electrode for electrolysis had a thickness of 0.52 mm and an opening ratio of 23.3%. A value, which is obtained by dividing the sum of perimeters of openings by the opening ratio, was 2.36.

[0148] The above electrode for electrolysis was used for reactivating the electrode decreased in activity. As the electrode decreased in activity, an electrode for electrolysis was produced in the same manner as in Comparative Example 1 and used in an electrolyzer of a production plant for 7.1 years by supplying power was used. The electrode was cut into pieces having a predetermined size (95 × 110 mm = 0.01045 m^2) and used as a base electrode. The base electrode was attached to the rib of an anode chamber of an anode cell by welding. A reduction amount of electrolysis voltage at a current density of 6 kA/m^2 increased by 35 mV based on that of Comparative Example 1. To the base electrode, the above electrode for electrolysis was attached by welding as a renewal electrode to produce an electrolyzer containing an electrode laminate.

[0149] Experiments of sodium chloride electrolysis by ion exchange membrane process were carried out by using the electrolyzer produced in Examples 8 and 9. The results are shown in Table 3.

[Table 3]

	FR	Thickness [mm]	SW [mm]	LW [mm]	A: Opening ratio [%]	B: Perimeter [mm]	B/A	Effect: ΔV
Example 8	○	0.56	1.6	3.0	17.5	57.7	3.30	33
Example 9	○	0.52	2.2	3.0	23.3	55.0	2.36	24

[0150] A reduction amount of electrolysis voltage at a current density of 6 kA/m^2 based on that of Comparative Example 1 was 33 mV in Example 8 and 24 mV in Example 9. It was found that both of them can reduce electrolysis voltage compared to Comparative Example 1, and that when an existing electrode decreased in activity is renewed, electrolysis performance is returned to the level before deterioration or further improved, in other words, the electrode can be reactivated.

Industrial Applicability

[0151] The electrode for electrolysis of the present invention can keep low voltage and power consumption during electrolysis and has practical strength. Because of this, the electrode for electrolysis of the present invention can be suitably used in the field of brine electrolysis and is useful particularly as an anode for sodium chloride electrolysis by ion exchange membrane process. The electrode for electrolysis of the present invention enables production of highly pure chlorine gas low in oxygen gas concentration for a long term at a low voltage and a low power consumption.

Reference Signs List

[0152]

1	Electrode
2,3	Opening
10	Electrode for electrolysis
20	Opening
100	Opening
100'	Opening
101	First imaginary center line
102	Second imaginary center line
a	Portion a
b	Portion b
200	Electrolyzer for electrolysis
210	Electrolyte solution
220	Container
230	Anode (electrode for electrolysis)
240	Cathode
250	Ion exchange membrane
260	Wiring
300	Electrode for electrolysis
310	Center-to-center distance SW of openings in minor-axis direction of mesh (the short width SW)
320	Center-to-center distance LW of openings in major-axis direction of mesh (the long width LW)
330	Second imaginary center line
340	Portion a
350	Portion b
360	Distance between openings in minor-axis direction of mesh

Claims

1. An electrode for electrolysis comprising
a conductive substrate formed of a porous metal plate, and
at least one catalyst layer formed on a surface of the conductive substrate, wherein
the electrode for electrolysis has a thickness of more than 0.5 mm and 1.2 mm or less; and
value C, which is obtained by dividing sum B of perimeters of openings of the electrode for electrolysis by opening ratio A of the electrode for electrolysis, is more than 2 and 5 or less.

2. The electrode for electrolysis according to claim 1, wherein the opening ratio A is 5% or more and less than 25%.

3. The electrode for electrolysis according to claim 1 or 2, wherein center-to-center distance SW of the openings in a minor-axis direction of a mesh is 1.5 or more and 3 or less; and center-to-center distance LW in a major-axis direction of the mesh is 2.5 or more and 5 or less.

4. The electrode for electrolysis according to any one of claims 1 to 3, wherein the electrode for electrolysis has a thickness of more than 0.5 mm and 0.9 mm or less.

5. The electrode for electrolysis according to any one of claims 1 to 4, wherein value E represented by the following formula (1) is 0.5 or more

$$E = B/(A \times (SW^2 + LW^2)^{1/2}) \qquad (1).$$

6. An electrolyzer comprising
an anode chamber comprising, as an anode, the electrode for electrolysis according to any one of claims 1 to 5,
a cathode chamber comprising a cathode, and

an ion exchange membrane isolating the anode chamber from the cathode chamber.

7. The electrolyzer according to claim 6, wherein the ion exchange membrane has a projection formed of a polymer constituting the ion exchange membrane on a surface facing the anode.

8. An electrode laminate comprising
the electrode for electrolysis according to any one of claims 1 to 3 and
a base electrode different from the electrode for electrolysis.

9. The electrode laminate according to claim 8, wherein the electrode for electrolysis has a thickness of more than 0.5 mm and 0.65 mm or less.

10. A method for renewing an electrode, comprising a step of welding the electrode for electrolysis according to any one of claims 1 to 3 on an existing electrode in an electrolyzer.

11. An electrode for electrolysis comprising
a conductive substrate formed of a porous metal plate, and
at least one catalyst layer formed on a surface of the conductive substrate, wherein
a shape of openings of the electrode for electrolysis is right-and-left symmetric about a first imaginary center line extending in a minor-axis direction of a mesh and up-and-down asymmetric about a second imaginary center line extending in a major-axis direction of the mesh; and
the electrode for electrolysis has a thickness of more than 0.5 mm and 1.2 mm or less.

12. The electrode for electrolysis according to claim 11, wherein when the openings each are partitioned in portion a and portion b by the second imaginary center line, a value obtained by dividing area Sa of the portion a by area Sb of the portion b is 1.15 or more and 2.0 or less.

13. The electrode for electrolysis according to claim 11 or 12, wherein a value obtained by dividing value St, which is obtained by subtracting a maximum size of the openings in the minor-axis direction of a mesh from center-to-center distance SW of the openings in the minor-axis direction of the mesh, by the SW is 0.4 or more.

Figure 1

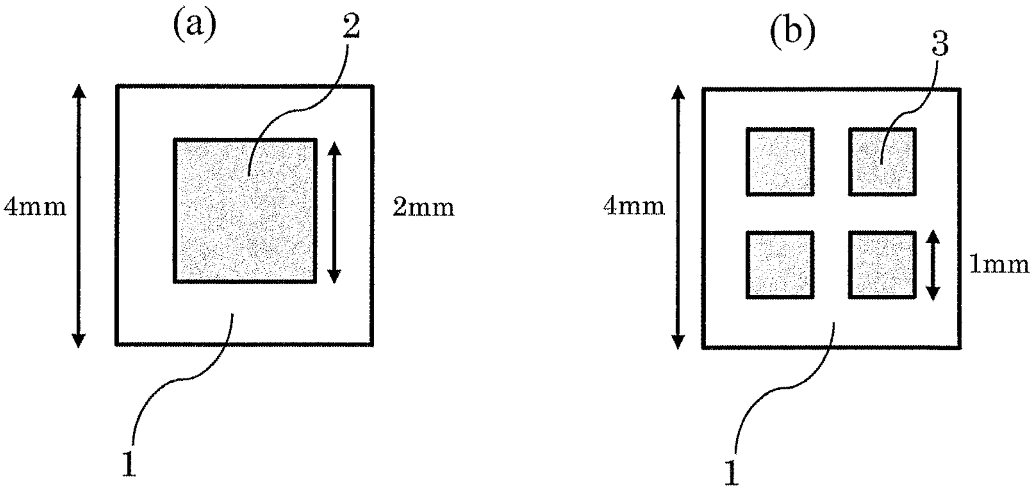


Figure 2

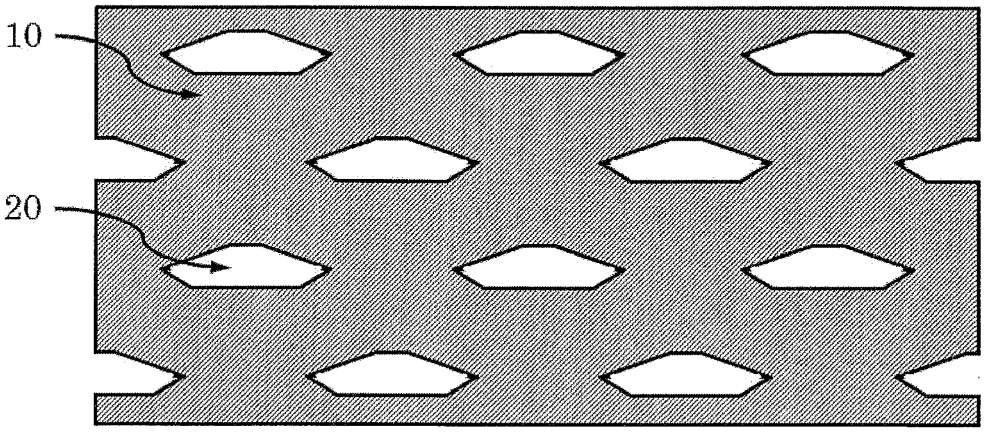


Figure 3

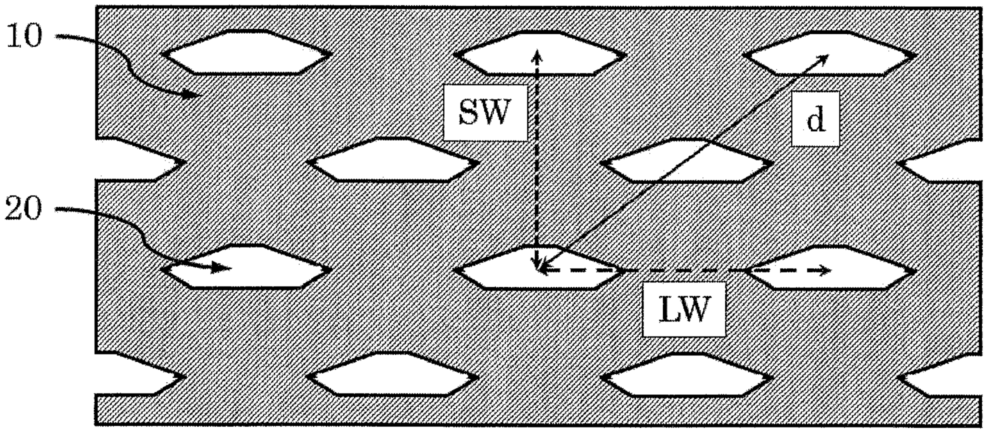


Figure 4

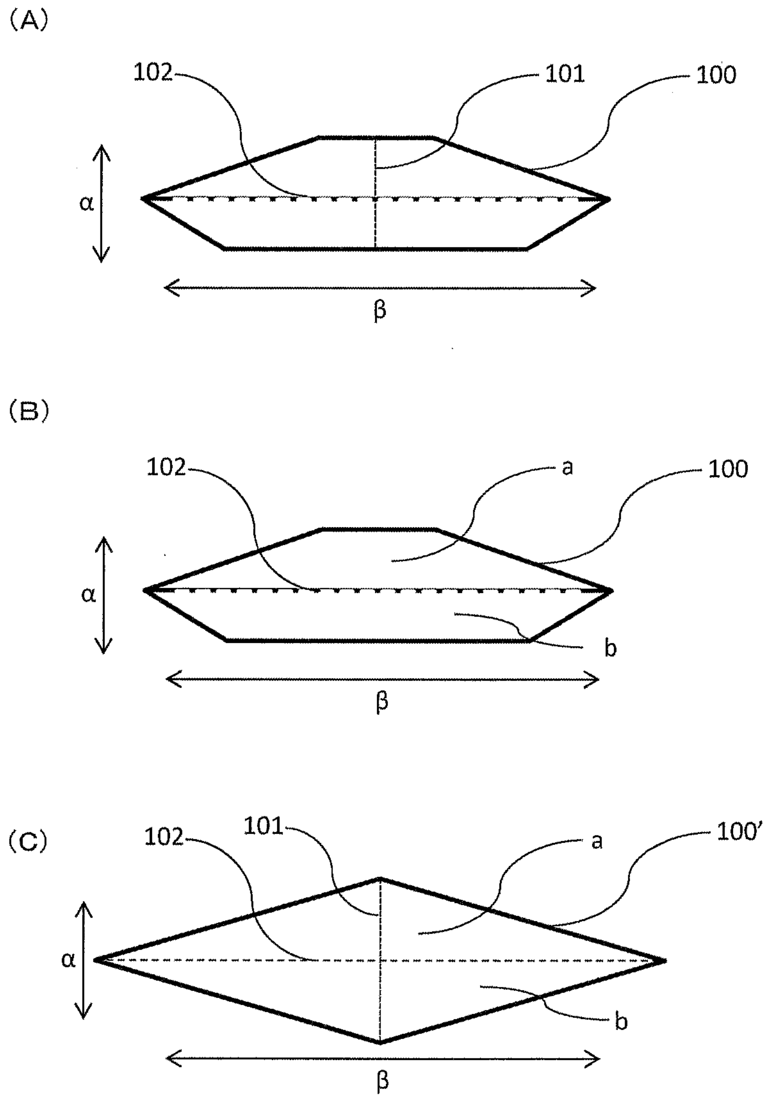


Figure 5

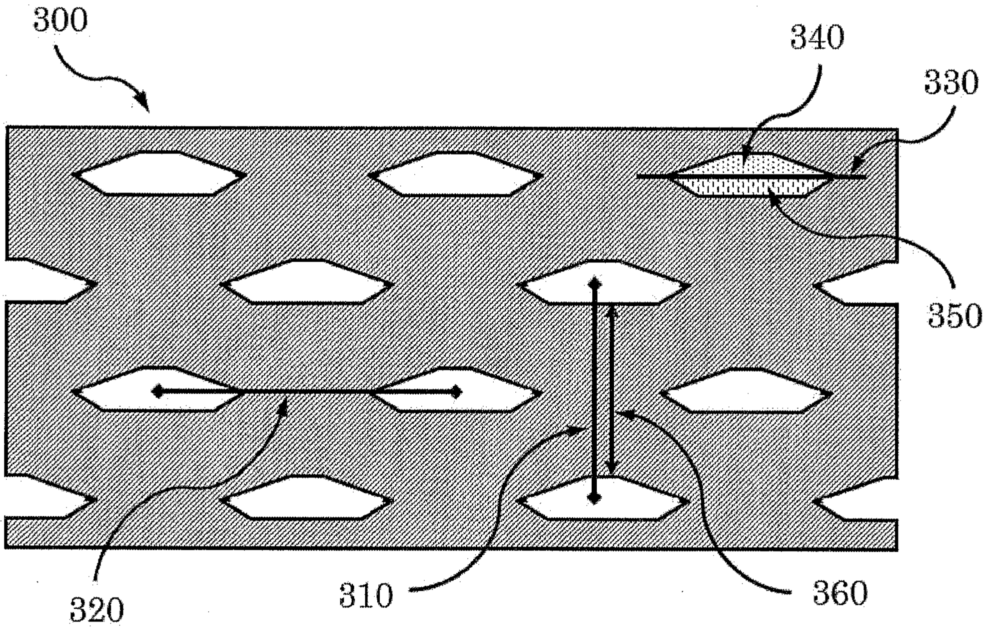
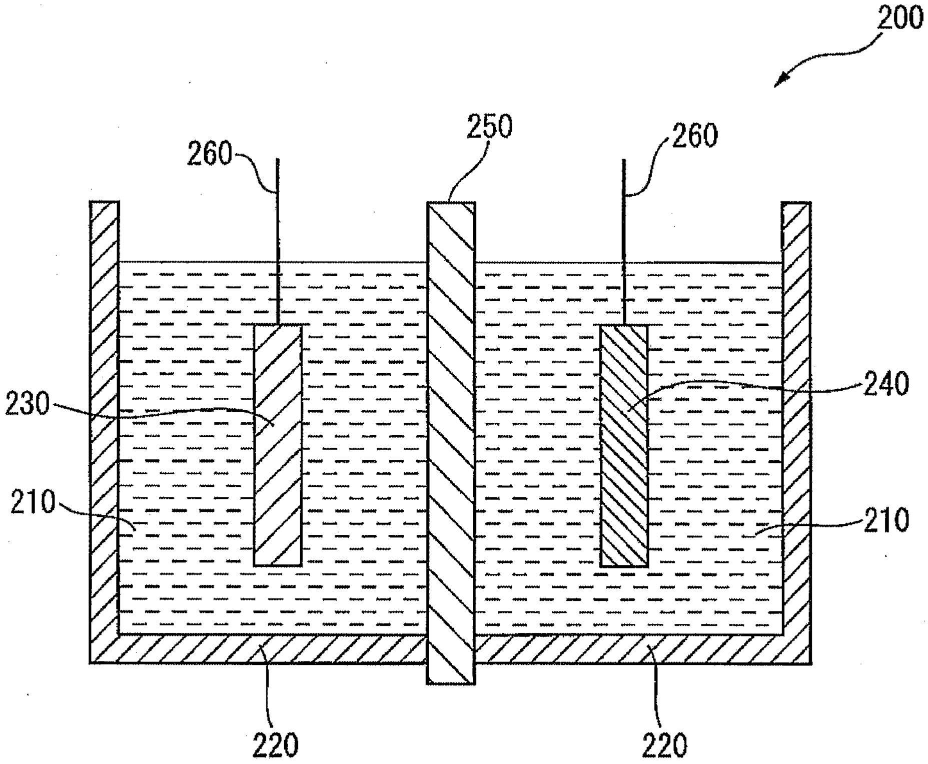


Figure 6



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/047365

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C25B11/03(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. C25B11/03

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2018
Registered utility model specifications of Japan	1996-2018
Published registered utility model applications of Japan	1994-2018

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2016-196674 A (TOSHIBA CORP.) 24 November 2016, entire text (Family: none)	1-13
A	JP 2010-174346 A (TOSOH CORP.) 12 August 2010, entire text (Family: none)	1-13

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
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Date of the actual completion of the international search
05 March 2018 (05.03.2018)

Date of mailing of the international search report
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Japan Patent Office
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/047365

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2015/108115 A1 (THYSSENKRUPP UHDE CHLORINE ENGINEERS LTD.) 23 July 2015, entire text & US 2016/0333488 A1, entire text & WO 2015/108115 A1 & EP 3095896 A1 & CN 105917027 A	1-13
A	JP 2007-23374 A (ASK:KK.) 01 February 2007, entire text (Family: none)	1-13
A	JP 62-44589 A (PERMELEC ELECTRODE LTD.) 26 February 1987, entire text & GB 2180556 A, entire text & DE 3625506 A & FR 2585372 A & NL 8601906 A & KR 10-1989-0002058 B1 & AU577957 B & SE 464250 B & IT 8648307 DO	1-13

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- WO 62502820 A **[0010]**
- JP 4453973 B **[0010]**
- WO 2015108115 A **[0010]**
- JP 4573715 B **[0097]**
- JP 4708133 B **[0097]**

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- **AIKAWA HIROAKI.** Survey Report on Technology Systematization, the eighth series. the independent administrative agency, the National Science Museum, 30 March 2007, 32 **[0011]**