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(71) Applicant: **Kabushiki Kaisha Toshiba**
Minato-ku
Tokyo (JP)

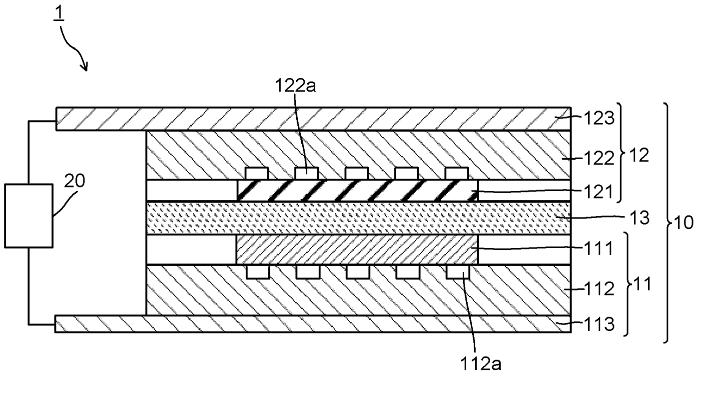
(72) Inventors:
- **Yamagiwa, Masakazu**
  Minato-ku, Tokyo (JP)
- **Ono, Akihiko**
  Minato-ku, Tokyo (JP)
- **Kofuji, Yusuke**
  Minato-ku, Tokyo (JP)
- **Kudo, Yuki**
  Minato-ku, Tokyo (JP)
- **Kitagawa, Ryota**
  Minato-ku, Tokyo (JP)
- **Mikoshiba, Satoshi**
  Minato-ku, Tokyo (JP)

(74) Representative: **Hoffmann Eitle**
Patent- und Rechtsanwälte PartmbB
Arabellastraße 30
81925 München (DE)

(54) CARBON DIOXIDE ELECTROLYSIS DEVICE AND METHOD OF OPERATING CARBON DIOXIDE ELECTROLYSIS DEVICE

(57) A carbon dioxide electrolysis device includes: a cathode configured to reduce carbon dioxide and thus form a carbon compound; an anode configured to oxidize water and thus generate oxygen; a cathode gas flow path facing on the cathode and configured to supply gas containing carbon dioxide; an anode solution flow path facing on the anode and configured to supply an electrolytic solution containing water; and a separator provided between the anode and the cathode. An aspect ratio of the cathode gas flow path is greater than 1 and 3 or less. In a cross-section along a direction perpendicular to a facing surface between the cathode and the cathode gas flow path in the cathode gas flow path, a fluid mean depth M of the cathode gas flow path and a depth h of the cathode gas flow path satisfy a formula: $h/8 \le M < h/4$.

FIG. 1



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Description

FIELD

[0001] Arrangements relate to a carbon dioxide electrolysis device.

BACKGROUND

[0002] In recent years, renewable energy such as solar power is desirably converted into not only electrical energy for use but also a storable and transportable resource in terms of both energy and environmental issues. This demand has advanced research and development of artificial photosynthesis technology, which uses sunlight to produce chemical substances like photosynthesis in plants. This technology has potential to store the renewable energy as storable fuel and is also expected to create value by producing chemical substances that can be used as industrial raw materials.

[0003] Known examples of a device that uses the renewable energy such as solar power to produce chemical substances, include an electrochemical reaction device having a cathode and an anode, the cathode being configured to reduce carbon dioxide (CO_2) generated from a power plant or waste treatment plant, and the anode being configured to oxidize water (H_2O). The cathode, for example, reduce carbon dioxide to produce carbon compounds such as carbon monoxide (CO). When such an electrochemical reaction device is fabricated in a cell form (also called an electrolysis cell), it may be effective to fabricate it in a form similar to a fuel cell, such as a polymer electric fuel cell (PEFC). The directly supply of carbon dioxide to a catalyst layer of the cathode, rapidly processes a carbon dioxide reduction reaction.

[0004] However, such a cell form has a problem similar to that of the PEFC arises. In other words, it is necessary to stably supply carbon dioxide to the cathode catalyst layer to fabricate the electrolysis cell that is resistant to failure and durable and to improve efficiency of carbon compound production.

RELEVANT REFERENCES

Patent Reference

[0005]

Reference1: US Patent No. 7659024
Reference 2: US Patent No. 7087337

BRIEF DESCRIPTION OF THE DRAWINGS

[0006]

FIG. 1 is a schematic diagram to explain a configuration example of a carbon dioxide electrolysis device.
FIG. 2 is a planar schematic diagram illustrating a structural example of a part of a flow path plate.
FIG. 3 is a cross-sectional schematic diagram illustrating a structural example of a part of the flow path plate.
FIG. 4 is a planar schematic diagram illustrating another structural example of the flow path plate.
FIG. 5 is a cross-sectional schematic diagram illustrating another structural example of a part of the flow path plate.
FIG. 6 is a cross-sectional schematic diagram illustrating still another structural example of a part of the flow path plate.
FIG. 7 is a cross-sectional schematic diagram illustrating yet another structural example of a part of the flow path plate.
FIG. 8 is a schematic diagram illustrating another configuration example of the carbon dioxide electrolysis device.
FIG. 9 is a flowchart to explain an operating method example of the carbon dioxide electrolysis device.
FIG. 10 is a flowchart to explain an operation example of a refresh operation step.
FIG. 11 is a diagram illustrating a relationship between a partial current density of carbon monoxide and a utilization ratio of carbon dioxide at a cathode.
FIG. 12 is a diagram illustrating a relationship between the partial current density of carbon monoxide and the utilization ratio of carbon dioxide at the cathode.

DETAILED DESCRIPTION

[0007] A problem to be solved by the present invention is to suppress a decrease in electrolysis efficiency of carbon dioxide electrolytic devices.

[0008] A carbon dioxide electrolysis device includes: a cathode configured to reduce carbon dioxide and thus form a carbon compound; an anode configured to oxidize water and thus generate oxygen; a cathode gas flow path facing on the cathode and configured to supply gas containing carbon dioxide; an anode solution flow path facing on the anode and configured to supply an electrolytic solution containing water; and a separator provided between the anode and the cathode. An aspect ratio of the cathode gas flow path is greater than 1 and 3 or less, the aspect ratio being defined by a ratio of a depth of the cathode gas flow path to a width of the cathode gas flow path. In a cross-section along a direction perpendicular to a facing surface between the cathode and the cathode gas flow path in the cathode gas flow path, a fluid mean depth M of the cathode gas flow path and a depth h of the cathode gas flow path satisfy a formula: $h/8 \leq M < h/4$, the fluid mean depth M being defined by a ratio of a circumferential length of the cathode gas flow path to a cross-sectional area of the cathode gas flow path.

[0009] Hereinafter, arrangements will be described with reference to the drawings. The drawings are schematic, and dimensions such as a thickness and a width of each component are sometimes different from actual ones. In each arrangement presented below, substantially the same components are denoted by the same reference signs, and a description thereof is sometimes partially omitted.

[0010] In this specification, "connection" includes not only direct connection but also indirect connection, unless otherwise specified.

[0011] FIG. 1 is a schematic diagram to explain a configuration example of a carbon dioxide electrolysis device. FIG. 1 illustrates a carbon dioxide electrolysis device 1 including an electrolysis cell 10.

[0012] The electrolysis cell 10 includes an anode part 11, a cathode part 12, and a separator 13 that separates the anode part 11 from the cathode part 12. The electrolysis cell 10 is, for example, sandwiched between a pair of support plates and further tightened with bolts or the like.

[0013] The anode part 11 includes an anode 111, an anode solution flow path 112a provided on a flow path plate 112, and an anode current collector 113.

[0014] The cathode part 12 includes a cathode 121, a cathode gas flow path 122a provided on a flow path plate 122, and a cathode current collector 123.

[0015] The anode 111 is an electrode (oxidation electrode) that promotes an oxidation reaction of water (H_2O) in an anode solution to produce oxygen (O_2) and hydrogen ions (H^+), or an oxidation reaction of hydroxide ions (OH^-) generated in the cathode part 12 to produce oxygen and water.

[0016] The anode 111 is disposed between the separator 13 and the flow path plate 112 to be in contact therewith. A first surface of the anode 111 is in contact with the separator 13. A second surface of the anode 111 is provided on an opposite side of the first surface of the anode 111 and faces the anode solution flow path 112a.

[0017] Compounds produced by the oxidation reaction of the anode 111 are different depending on types of oxidation catalysts and other factors. When an electrolytic solution is used as the anode solution, the anode 111 is preferably mainly composed of a catalyst material (anode catalyst material) capable of oxidizing water (H_2O) to produce oxygen and hydrogen ions, or oxidizing hydroxide ions (OH^-) to produce water and oxygen, and capable of decreasing an overvoltage of such reactions. Such catalyst materials include metals such as platinum (Pt), palladium (Pd), and nickel (Ni), alloys and intermetallic compounds containing these metals, binary metal oxides such as manganese oxide (Mn-O), iridium oxide (Ir-O), nickel oxide (Ni-O), cobalt oxide (Co-O), iron oxide (Fe-O), tin oxide (Sn-O), indium oxide (In-O), ruthenium oxide (Ru -O), lithium oxide (Li-O), and lanthanum oxide (La-O), ternary metal oxides such as Ni-Co-O, Ni-Fe-O, La-Co-O, Ni-La-O, and Sr-Fe-O, quaternary metal oxides such as Pb-Ru-Ir-O and La-Sr-Co-O, and metal complexes such as Ru complexes and Fe complexes.

[0018] The anode 111 is preferably equipped with a substrate (support) having a structure that enables a movement of the anode solution and ions between the separator 13 and the anode solution flow path 112a, such as a mesh material, a punching material, or a porous structure such as a porous member. The substrate having the porous structure also includes the substrate with relatively large pores, such as a metal fiber sintered compact. The substrate may be composed of metals such as titanium (Ti), nickel (Ni), and iron (Fe) or a metal material such as an alloy containing at least one of these metals (for example, SUS), or may be composed of the anode catalyst materials described above. When oxides are used as the anode catalyst material, a catalyst layer is preferably formed by attaching or laminating the anode catalyst material to a surface of the substrate made of the metal material described above. The anode catalyst material preferably has a shape such as nanoparticles, nanostructures, or nanowires to enhance the oxidation reaction. The nanostructures are structures with nanoscale irregularities formed on a surface of the catalyst material. The oxidation catalyst does not necessarily have to be provided on the oxidation electrode. An oxidation catalyst layer provided other than the oxidation electrode may be electrically connected to the oxidation electrode.

[0019] The cathode 121 is an electrode (reduction electrode) that generates reduction reactions of carbon dioxide and reduction products to produce carbon compounds. Examples of the carbon compounds include carbon monoxide (CO), formic acid (HCOOH), methane (CH4), ethane (C_2H_6), ethylene (C_2H_4), methanol (CH_3OH), acetic acid (CH_3COOH), ethanol (C_2H_5OH)), formaldehyde (HCHO), propanol (C_3H_7OH), and ethylene glycol ($C_2H_6O_2$). Along with the reduction reaction of carbon dioxide, the reduction reaction at the cathode 121 may include a side reaction that generates a water reduction reaction to produce hydrogen (H2).

[0020] The cathode 121 is preferably composed of an ion-conductive substance in addition to an electrode substrate and a metal catalyst supported on a carbon material. The ion-conductive substance exhibits an action of transferring ions between metal catalysts contained in layers and thus exerts effects of enhancing the electrode activity. A cation exchange resin or anion exchange resin is preferably used as the above ion-conductive substance.

[0021] The support for the metal catalyst preferably has the porous structure. In addition to the above materials, applicable materials include, for example, carbon blacks such as Ketjen black and Vulcan XC-72, activated carbon, carbon nanotubes, and the like. By having the porous structure, an area of an active surface that contributes to the oxidation-reduction reaction can be increased, thus increasing conversion efficiency.

[0022] The catalyst layer itself formed on the substrate as well as the support preferably has the porous structure and has a large number of relatively large pores. Specifically, in terms of a pore size distribution of the catalyst layer measured by a mercury intrusion method, a frequency of pore distribution is preferably maximized in a range of 5 μm or more and 200 μm or less in diameter. In this case, gas diffuses quickly throughout the catalyst layer, and reduction products are easily discharged outside the catalyst layer through this pathway, resulting in an efficient electrode.

[0023] A gas diffusion layer is preferably provided on the electrode substrate supporting the catalyst layer to efficiently supply carbon dioxide to the catalyst layer. The gas diffusion layer is formed by a conductive porous member. The gas diffusion layer is preferably formed by a water-repellent porous member because amounts of water produced by the reduction reaction and water that has moved from an oxidation side can be lowered, allowing the water to drain through a reduction flow path and increasing the percentage of carbon dioxide gas in the porous member.

[0024] When a thickness of the gas diffusion layer is extremely small, uniformity on a cell surface is impaired, which is not desirable. On the other hand, when the thickness is extremely large, a member cost increases and efficiency decreases due to the increase in gas diffusion resistance, which is not desirable. A denser diffusion layer (mesoporous layer (MPL)) is more preferably provided between the gas diffusion layer and the catalyst layer to further improve diffusibility, as it changes the water repellency and porosity to promote gas diffusibility and liquid component drainage.

[0025] The metal catalysts supported on the above support include materials that decrease activation energy for the reduction of hydrogen ions and carbon dioxide. In other words, metal materials that decrease the overvoltage in the reduction reaction of carbon dioxide to produce carbon compounds are included. For example, it is preferred to use at least one metal selected from the group consisting of gold (Au), silver (Ag), copper (Cu), platinum (Pt), palladium (Pd), nickel (Ni), (Co), iron (Fe), manganese (Mn), titanium (Ti), cadmium (Cd), zinc (Zn), indium (In), gallium (Ga), lead (Pb), and tin (Sn), and metal oxide or alloys containing these metals. For example, at least one of copper, gold, and silver is preferably used. For example, metal complexes such as ruthenium (Ru) complexes or rhenium (Re) complexes, can also be used as reduction catalysts without being limited to the above. A plurality of materials may also be mixed. Various shapes can be applied to the metal catalyst, such as plate, mesh, wire, particle, porous, thin-film, and island shapes.

[0026] When metal nanoparticles are applied to the metal catalyst, an average diameter is preferably 1 nm or more and 15 nm or less, more preferably 1 nm or more and 10 nm or less, and even more preferably 1 nm or more and 5 nm or less. Meeting these conditions is desirable because a surface area of the metal per catalyst weight becomes larger, and a small amount of metal is required to exhibit high activity.

[0027] The anode 111 and cathode 121 can be connected to a power supply 20. The power supply 20 applies a voltage between the anode 111 and cathode 121. Examples of the power supply 20 are not limited to ordinary system power supplies or batteries but may include power sources that supply power generated by renewable energy sources such as solar cells or wind power. The power supply 20 may further include a power controller that adjusts output of the above power supply to control the voltage between the anode 111 and cathode 121. The power supply 20 may be provided outside the carbon dioxide electrolysis device 1.

[0028] The anode solution flow path 112a has a function of supplying the anode solution to the anode 111. The anode solution flow path 112a is formed by pits (grooves/recesses) provided in the flow path plate 112. The flow path plate 112 has an inlet and an outlet port (both not illustrated) connected to the anode solution flow path 112a, and the anode solution is introduced and discharged by a pump (not illustrated) through these inlet and outlet ports. The anode solution is distributed in the anode solution flow path 112a to be in contact with the anode.

[0029] An aqueous solution containing metal ions (electrolytic solution) can be used as the anode solution. By using the electrolytic solution containing metal ions, the electrolysis efficiency can be increased. The aqueous solution can be, for example, aqueous solutions containing phosphate ions (PO_4^{2-}), borate ions (BO_3^{3-}), sodium ions (Na^+), potassium ions (K^+), calcium ions (Ca^{2+}), lithium ions (Li^+), cesium ions (Cs^+), magnesium ions (Mg^{2+}), chloride ions (Cl^-), hydrogen carbonate ions (HCO_3^-), carbonate ions (CO_3^{2-}), and other aqueous solutions. Other aqueous solutions containing $LiHCO_3$, $NaHCO_3$, $KHCO_3$, $CsHCO_3$, phosphoric acid, boric acid, and so on may also be used.

[0030] The cathode gas flow path 122a faces a first surface of the cathode 121. The cathode gas flow path 122a has a function of supplying gas containing carbon dioxide to the cathode 121. For example, the cathode gas flow path 122a can be connected to a carbon dioxide supply source that supplies the gas containing carbon dioxide. The carbon dioxide supply source can be, for example, a power plant, waste treatment plant, or other facilities. The cathode gas flow path 122a is formed by pits (grooves/recesses) provided in the flow path plate 122. The flow path plate 122 has an inlet and an outlet port (both not illustrated) connected to the cathode gas flow path 122a, and the gas is introduced and discharged by a pump (not illustrated) through these inlet and outlet ports.

[0031] It is preferable to use materials for the flow path plates 112 and 122 that have low chemical reactivity and high electrical conductivity. Examples of such materials include, for example, metal materials such as Ti and SUS, carbon, and the like. The flow path plates 112 and 122 have the inlet and outlet ports for each flow path, as well as screw holes for tightening, although these are not illustrated in the drawing. Packing, not illustrated, is sandwiched between a front and back of each flow path plate as necessary. Although the flow path plates 112 and 122 are mainly formed from a single member, they may also be formed from different members and laminated together. Furthermore, hydrophilic and water-repellent functions may be added by applying surface treatment to part or all thereof.

[0032] The flow path plate 122 can have a land in contact with the cathode 121 for electrical connection with the cathode 121. A shape of the cathode gas flow path 122a can be adjacent to a columnar land, a serpentine shape where a thin flow path is folded or the like, but any shape with a cavity can be used. The cathode gas flow path 122a is preferably constituted by a plurality of flow paths connected in parallel, a serpentine flow path, or a combination thereof because the uniformity of the gas to be supplied to the cathode 121 can be enhanced and the uniformity of an electrolytic reaction can be enhanced.

[0033] FIG. 2 is a planar schematic diagram illustrating a structural example of a part of the flow path plate 122. FIG. 2 illustrates an X-Y plane of the flow path plate 122 including an X-axis and a Y-axis orthogonal to the X-axis. In FIG. 2, only a superposition of the flow path plate 122 and the cathode 121 is schematically illustrated. FIG. 3 is a cross-sectional schematic diagram illustrating a structural example of a part of the flow path plate 122. FIG. 3 illustrates a Y-Z plane of the flow path plate 122 including the Y-axis and a Z-axis orthogonal to the Y-axis and X-axis. The Z-axis direction is a thickness direction of the flow path plate 122.

[0034] The flow path plate 122 has a surface 241, a surface 242, and the cathode gas flow path 122a. The surface 241 is in contact with the cathode 121. The surface 242 is provided on an opposite side of the surface 241 and in contact with the cathode current collector 123. The flow path plate 122 illustrated in FIG. 2 and FIG. 3 has a rectangular parallelepiped shape. A three-dimensional shape of the flow path plate 122 is not limited to the rectangular parallelepiped shape.

[0035] The cathode gas flow path 122a faces the gas diffusion layer of the cathode 121. The cathode gas flow path 122a is connected to the inlet and outlet ports. The inlet port is provided for introducing the gas containing carbon dioxide into the cathode gas flow path 122a. The outlet port is provided for discharging the gas containing carbon dioxide from the cathode gas flow path 122a and for discharging products of the reduction reaction from the cathode gas flow path 122a.

[0036] The cathode gas flow path 122a illustrated in FIG. 2 extends in a serpentine shape along the surface 241. The cathode gas flow path 122a may also extend in a comb-teeth or spiral shape along the surface 241 without being limited to the serpentine shape. The cathode gas flow path 122a includes a space formed by, for example, a groove or opening provided at the flow path plate 122.

[0037] The carbon dioxide gas may be supplied in a dry state. A carbon dioxide concentration in the gas supplied to the cathode gas flow path 122a does not have to be 100%. In this case, it is also possible to reduce the gas containing carbon dioxide emitted from each of various facilities, although the efficiency will decrease.

[0038] The flow path plates 112 and 122 preferably have the same shape as each other. This can improve uniformity of the reaction. The flow path plates 112 and 122 may have different shapes from each other.

[0039] The anode current collector 113 is in contact with a surface of the flow path plate 112 opposite to a contact surface with the anode 111. The anode current collector 113 is electrically connected to the anode 111. The anode current collector 113 preferably contains a material with low chemical reactivity and high electrical conductivity. Such materials include metal materials such as Ti and SUS, carbon, and the like.

[0040] The cathode current collector 123 is in contact with a surface of the flow path plate 122 opposite to a contact surface with the cathode 121. The cathode current collector 123 is electrically connected to the cathode 121. The cathode current collector 123 preferably contains a material with low chemical reactivity and high electrical conductivity. Such materials include metal materials such as Ti and SUS, carbon, and the like.

[0041] The separator 13 is provided between the anode 111 and the cathode 121. The separator 13 is formed of an ion-exchange membrane or the like that can move ions between the anode and the cathode and can separate the anode part from the cathode part. For example, cation-exchange membranes such as Nafion and Fremion, and anion-exchange membranes such as Neosepta, Selemion, and Sustenion can be used as the ion-exchange membrane. When an alkaline solution is used as the electrolytic solution and the moving of mainly hydroxide ions (OH^-) is mainly assumed, the separator is preferably formed of the anion-exchange membrane. The ion-exchange membrane may be formed by using a membrane with a hydrocarbon basic structure or a membrane with an amine group. In addition to the ion-exchange membrane, salt bridges, glass filters, porous polymer membranes, porous insulating materials, and so on may be applied to the separator as long as the material is capable of moving ions between the anode and the cathode. However, when gas distribution occurs between the cathode and anode parts, circular reactions due to reoxidation of reduction products may occur. Therefore, it is preferable to have less gas exchange between the cathode and anode parts. Therefore, care should be taken when using a porous thin membrane as the separator.

[0042] Next, an operation example of the carbon dioxide electrolysis device of the arrangement will be explained. Here, the case where the carbon dioxide electrolysis device 1 illustrated in FIG. 1 produces carbon monoxide as a carbon compound is mainly explained, but the carbon compound as the reduction product of carbon dioxide is not limited to carbon monoxide. The reduction product, carbon monoxide, may be further reduced to produce organic compounds as described above. The electrolysis cell 10 is preferably used when producing solution carbon compounds. A reaction process by the electrolysis cell 10 may be the case mainly producing hydrogen ions (H^+) or the case mainly producing hydroxide ions (OH^-) but is not limited to either of these reaction processes.

[0043] The reaction process is described mainly for the oxidation of water (H_2O) to produce hydrogen ions (H^+). When the current is supplied from the power supply 20 between the anode 111 and cathode 121, the oxidation reaction of water (H_2O) occurs at the anode 111 in contact with the anode solution. Specifically, as shown in Equation (1) below, H_2O contained in the anode solution is oxidized to produce oxygen (O_2) and hydrogen ions (H^+).

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \ldots \qquad (1)$$

[0044] H^+ produced at the anode 111 moves through the electrolytic solution present in the anode 111 and the separator 13 to reach near the cathode 121. Electrons (e^-) in accordance with the current supplied to the cathode 121 from the power supply 20 and H^+ that moves near the cathode 121 causes the reduction reaction of carbon dioxide (CO_2). Specifically, as shown in Equation (2) below, carbon dioxide supplied to the cathode 121 from the cathode gas flow path 122a is reduced to produce carbon monoxide. Hydrogen is also produced when hydrogen ions receive electrons, as shown in Equation (3) below. In this case, hydrogen may be produced simultaneously with carbon monoxide.

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \ldots \qquad (2)$$

$$2H^+ + 2e^- \rightarrow H_2 \ldots \qquad (3)$$

[0045] Next, a reaction process when carbon dioxide (CO_2)is mainly reduced to produce hydroxide ions (OH^-) is described. When the current is supplied from the power supply 20 between the anode 111 and the cathode 121, water (H_2O) and carbon dioxide (CO_2)are reduced near the cathode 121 to produce carbon monoxide (CO) and hydroxide ions (OH^-), as shown in Equation (4) below. In addition, hydrogen is produced when water receives electrons as shown in Equation (5) below. At this time, hydrogen may be produced simultaneously with carbon monoxide. The hydroxide ions (OH^-) produced by these reactions diffuse near the anode 111, and as shown in Equation (6) below, hydroxide ions (OH^-) are oxidized to produce oxygen (O_2).

$$2CO_2 + 2H_2O + 4e^- \rightarrow 2CO + 4OH^- \ldots \qquad (4)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \ldots \qquad (5)$$

$$4OH^- \rightarrow 2H_2O + O_2 + 4e^- \ldots \qquad (6)$$

[0046] In the electrolysis cell 10 illustrated in FIG. 1, the anode solution and ions are supplied from the separator 13, and carbon dioxide gas is supplied from the cathode gas flow path 122a.

[0047] The carbon dioxide electrolysis device 1 can not only specialize in carbon dioxide reduction, but can also produce carbon dioxide reduction products and hydrogen, for example, by having carbon monoxide and hydrogen in any ratio, such as 1:2, and then producing methanol in a subsequent chemical reaction.

[0048] Since hydrogen is an inexpensive and readily available raw material from water electrolysis and fossil fuels, it is not necessary to have a large ratio of hydrogen. From these points of view, a ratio of carbon monoxide to hydrogen of at least 1 or more, and preferably 1.5 or more, is preferable in terms of economic efficiency and environmental friendliness.

[0049] The cathode gas flow path 122a is preferably shallow in terms of supplying carbon dioxide to the gas diffusion layer. On the other hand, when the cathode gas flow path 122a is narrow, pressure loss increases in the cathode gas flow path 122a, which is not desirable in terms of energy loss in the gas supply. Furthermore, when salts are precipitated due to a reaction between metal ions in the anode solution and the carbon dioxide gas, and the salts solidify at a boundary with the gas diffusion layer of the cathode gas flow path 122a, the shallow flow path will be closed and prevent the carbon dioxide gas from spreading to an entire electrode surface, which may cause failure to affect durability.

[0050] In one example of a conventional fuel cell, it is known that a groove is formed on an inner bottom surface of a flow path to store foreign matters (water droplets) to prevent the flow path from being blocked by the foreign matters (water droplets). However, in the case of the carbon dioxide electrolysis device, since the precipitated salts solidify near a facing surface between the cathode 121 and the cathode gas flow path 122a, forming a groove on the inner bottom surface is not effective in preventing the blockage.

[0051] On the other hand, in the carbon dioxide electrolysis device of this arrangement, a cross-sectional shape of the cathode gas flow path 122a is controlled to prevent the blockage of the flow path. An aspect ratio of the cathode gas flow path 122a is preferably greater than 1 and 3 or less. The aspect ratio of the cathode gas flow path 122a is defined by a ratio of a depth h of the cathode gas flow path 122a to a width W of the cathode gas flow path 122a in the X-axis or Y-axis direction.

[0052] When the aspect ratio is less than 1, the flow path may be blocked due to the salt precipitation. When the aspect ratio exceeds 3, the flow path plate 122 needs to be thickened, which increases material and processing costs. The aspect ratio is more preferably 2 or more and 3 or less.

[0053] A fluid mean depth M of the cathode gas flow path 122a and the depth h of the cathode gas flow path 122a preferably satisfy a formula (A) below.

A formula:

$$h/8 \leq M < h/4 \qquad (A)$$

[0054] The fluid mean depth M of the cathode gas flow path 122a is defined by a cross-sectional area Ac of the cathode gas flow path 122a to a circumferential length S of the cathode gas flow path 122a. The circumferential length S may be calculated by (width W × 2) + (depth h × 2). Even if the aspect ratio of the cathode gas flow path 122a is large, when the fluid mean depth M of the cathode gas flow path 122a is small, salts may precipitate in the cathode gas flow path 122a and easily block the cathode gas flow path 122a.

[0055] When the fluid mean depth M is less than h/8, the flow path may be blocked due to the salt precipitation. When the fluid mean depth M is h/4 or more, a utilization ratio of carbon dioxide may decrease. The fluid mean depth M is more preferably h/7.9 or more and h/6 or less.

[0056] The depth h, the width W, the circumferential length S, and the fluid mean depth M can be measured by the following method. A cross-section of the flow path plate 122 in a perpendicular direction (X-axis direction in FIG. 2) to a long direction (Y-axis direction in FIG. 2) of the cathode gas flow path 122a is cut out at an arbitrary position, and the cross-section is observed with a microscope, for example, to measure each parameter. Also, as a non-destructive inspection method, for example, neutron radiography can be used to visualize an inside of the flow path plate. It is preferable to calculate these values by averaging values at multiple locations.

[0057] The enough deep of the cathode gas flow path 122a to meet the above conditions can form a space in a depth direction of the cathode gas flow path 122a where the gas can be diverted. This is desirable in terms of eliminating blockage of gas supply during salt precipitation and makes it easier to supply the carbon dioxide gas to the entire surface of the cathode 121 even if salts precipitate at a part of the cathode gas flow path 122a, and is therefore less prone to failure and more desirable in terms of durability. Thus, the decrease in the electrolysis efficiency can be prevented, and the carbon dioxide electrolysis device that is highly efficient and can be operated for a long time can be provided.

[0058] The shape of the cathode gas flow path 122a is not limited to the shapes illustrated in FIG. 2 and FIG. 3. Other examples of the shape of the cathode gas flow path 122a are described below.

[0059] FIG. 4 is a planar schematic diagram illustrating another structural example of the flow path plate 122. FIG. 4 illustrates the X-Y plane of the flow path plate 122. The flow path plate 122 illustrated in FIG. 4 differs from the flow path plate 122 illustrated in FIG. 2 in that the cathode gas flow path 122a has a plurality of flow path parts 244 connected in parallel in the X-Y plane. The other parts are the same as the flow path plate 122 illustrated in FIG. 2, so the above explanation can be used as appropriate.

[0060] The plurality of flow path parts 244 extend along the long direction (Y-axis direction in FIG. 4) of the cathode gas flow path 122a. FIG. 4 illustrates an example of two flow path parts 244 connected in parallel for each fold of the cathode gas flow path 122a, but the number of flow path parts 244 is not limited to the number illustrated in FIG. 4. The width W of the cathode gas flow path 122a illustrated in FIG. 4 is defined by a width of one flow path part 244.

[0061] FIG. 5 is a cross-sectional schematic diagram illustrating still another structural example of a part of the flow path plate 122. FIG. 5 illustrates the Y-Z plane of the flow path plate 122. The flow path plate 122 illustrated in FIG. 5 differs from the flow path plate 122 illustrated in FIG. 3 in that the cathode gas flow path 122a has regions 122a1 and 122a2 in an X-Z cross-section. The other parts are the same as the flow path plate 122 illustrated in FIG. 3, so the above explanation can be used as appropriate.

[0062] The region 122a1 faces the cathode 121 and has an inner wall surface 246. A cross-sectional shape of the region 122a1 illustrated in FIG. 5 is a rectangle, but the shape of the region 122a1 is not limited to the shape in FIG. 5.

[0063] The region 122a2 is provided between the region 122a1 and an inner bottom surface 245 of the cathode gas flow path 122a and has an inner wall surface 247. A cross-sectional shape of the region 122a2 illustrated in FIG. 5 is a rectangle, but the shape of the region 122a2 is not limited to the shape in FIG. 5.

[0064] A width W2 in the X-axis direction of the region 122a2 is wider than a width W1 in the X-axis direction of the region 122a1. In the flow path plate 122 illustrated in FIG. 5, a space for the carbon dioxide gas to be diverted can be increased, and thus the blockage of the cathode gas flow path 122a due to the salt precipitation can be prevented by making the width W2 wider than the width W1. The width W of the cathode gas flow path 122a illustrated in FIG. 5 is defined by the width W1. The fluid mean depth M is defined by the circumferential length of the cathode gas flow path 122a having the shape illustrated in FIG. 5, taking into account both the width W1 and the width W2.

[0065] FIG. 6 is a cross-sectional schematic diagram illustrating still another structural example of a part of the flow path plate 122. FIG. 6 illustrates the Y-Z plane of the flow path plate 122. Compared to the flow path plate 122 illustrated in FIG. 5, the flow path plate 122 illustrated in FIG. 6 has a different shape of the region 122a2 in the X-Z cross-section. The other parts are the same as the flow path plate 122 illustrated in FIG. 5, so the above explanation can be used as appropriate.

[0066] A cross-sectional shape of the region 122a2 illustrated in FIG. 6 is a square, but the shape of the region 122a2 is not limited to the shape in FIG. 6. In FIG. 6, a cross-sectional area of the region 122a2 is larger than that of the region 122a1. This allows for a larger space for the carbon dioxide gas to be diverted and prevents the blockage of the cathode gas flow path 122a due to the salt precipitation. The width W of the cathode gas flow path 122a illustrated in FIG. 6 is defined by the width W1. The fluid mean depth M is defined by the circumferential length of the cathode gas flow path 122a having the shape illustrated in FIG. 6, taking into account both the width W1 and the width W2.

[0067] FIG. 7 is a cross-sectional schematic diagram illustrating yet another structural example of a part of the flow path plate 122. FIG. 7 illustrates the Y-Z plane of the flow path plate 122. The flow path plate 122 illustrated in FIG. 7 differs from the flow path plate 122 illustrated in FIG. 3 in that the cathode gas flow path 122a has the regions 122a1 and 122a2 in the X-Z cross-section, the inner wall surface 246 of the region 122a1 is hydrophilic, and the inner wall surface 247 and the inner bottom surface 245 of the region 122a2 are water repellent. The other parts are the same as the flow path plate 122 illustrated in FIG. 3, so the above explanation can be used as appropriate.

[0068] A contact angle with water at the hydrophilic inner wall surface 246 is, for example, more than 0 degrees and 90 degrees or less. The hydrophilic inner wall surface 246 can be formed using a flow path layer containing, for example, a hydrophilic material. The hydrophilic inner wall surface 246 may also be formed by applying a hydrophilic treatment to the flow path layer containing a material applicable to the flow path plate 122.

[0069] A contact angle with water at the water-repellent inner wall surface 247 is, for example, 100 degrees or more and less than 180 degrees. The water-repellent inner wall surface 247 can be formed using a flow path layer containing, for example, a water-repellent material. The water-repellent inner wall surface 247 may also be formed by applying a water-repellent treatment to the flow path layer containing the material applicable to the flow path plate 122.

[0070] A thickness (length in the Z-axis direction) of the region 122a1 is not particularly limited, but is preferably half the depth h of the cathode gas flow path 122a or more, for example.

[0071] In the cathode gas flow path 122a illustrated in FIG. 7, for example, when metal ions in the anode solution flow into the cathode gas flow path 122a, the anode solution tends to flow into the region 122a1 by forming the hydrophilic inner wall surface 246 and the water-repellent inner wall surface 247. Therefore, the salt precipitation can be prevented in the region 122a2, and the blockage of the cathode gas flow path 122a due to the salt precipitation can be prevented. The structure illustrated in FIG. 7 may be combined with the structure illustrated in FIG. 5 or FIG. 6 as appropriate.

(Second Arrangement)

[0072] FIG. 8 is a schematic diagram illustrating another configuration example of the carbon dioxide electrolysis device. The carbon dioxide electrolysis device 1 illustrated in FIG. 8 includes the electrolysis cell 10, an anode solution supply system 100 that supplies an anode solution to the electrolysis cell 10, a gas supply system 300 that supplies carbon dioxide (CO_2)gas to the electrolysis cell 10, a product collection system 400 that collects products produced by a reduction reaction in the electrolysis cell 10, a control system 500 that detects types and amounts of the collected products as well as controls the products and a refresh operation, a waste solution collection system 600 that collects a waste solution of the anode solution, and a refresh material supply 700 that recovers the anode, cathode, and so on of the electrolysis cell 10. Components necessary for the refresh operation do not necessarily have to be provided.

[0073] The electrolysis cell 10 corresponds to the electrolysis cell 10 illustrated in FIG. 1. The explanation of each component of the electrolysis cell 10 in the first arrangement can be used as appropriate.

[0074] In FIG. 8, the power supply 20 that applies current to the anode 111 and the cathode 121 is provided. The power supply 20 is connected to the anode current collector 113 and the cathode current collector 123 through a current introduction member. The power supply 20 is not limited to an ordinary system power supply, batteries, and the like, but may also have a power source that supplies power generated by renewable energy sources such as solar cells and wind power. The power supply 20 may have the above power source, a power controller that adjusts output of the power source to control a voltage between the anode 111 and the cathode 121, or the like.

[0075] The anode solution is supplied as an electrolytic solution from the anode solution supply system 100 to the anode solution flow path 112a of the anode part 11. The anode solution supply system 100 circulates the anode solution so that the anode solution is distributed in the anode solution flow path 112a. The anode solution supply system 100 has a pressure controller 101, an anode solution tank 102, a flow rate controller (pump) 103, a reference electrode 104, and a pressure gauge 105, and is configured such that the anode solution circulates in the anode solution flow path 112a. The anode solution tank 102 is connected to a gas component collection unit, not illustrated, which collects oxygen (O_2) and other gas components contained in the circulating anode solution. The anode solution is introduced into the anode solution flow path 112a with the flow rate and pressure controlled in the pressure controller 101 and flow rate controller 103.

[0076] The CO_2 gas is supplied to the cathode gas flow path 122a from the gas supply system 300. The gas supply system 300 has a CO_2 gas cylinder 301, a flow rate controller 302, a pressure gauge 303, and a pressure controller 304. The CO_2 gas is introduced into the cathode gas flow path 122a with the flow rate and pressure controlled in the flow rate controller 302 and pressure controller 304. The gas supply system 300 is connected to the product collection system 400 that collects products in the gas distributed through the cathode gas flow path 122a. The product collection system 400 has a gas-liquid separation unit 401 and a product collection unit 402. Reduction products such as CO and H_2 contained in the gas distributed through the cathode gas flow path 122a are accumulated in the product collection unit 402 through the gas-liquid separation unit 401.

[0077] The anode solution circulates in the anode solution flow path 112a during the electrolytic reaction operation as described above. During the refresh operation of the electrolysis cell 10, described below, the anode solution is discharged into the waste solution collection system 600 so that the anode 111 and the anode solution flow path 112a are exposed from the anode solution.

[0078] The waste solution collection system 600 has a waste solution collection tank 601 connected to the anode solution flow path 112a. A waste solution of the anode solution is collected in the waste solution collection tank 601 by opening and closing not-illustrated valves. The opening and closing of the valves and other operations are collectively controlled by the control system 500. The waste solution collection tank 601 also functions as a collection unit for a rinse solution supplied from the refresh material supply 700. Furthermore, gaseous substances supplied from the refresh material supply 700 and containing some liquid substances are also collected in the waste solution collection tank 601 as necessary.

[0079] The refresh material supply 700 includes a gaseous substance supply system 710 and a rinse solution supply system 720. The rinse solution supply system 720 can be omitted in some cases. The gaseous substance supply system 710 has a gas tank 711 that serves as a supply source for gaseous substances such as air, carbon dioxide, oxygen, nitrogen, argon, and a pressure controller 712 that controls a supply pressure of the gaseous substances. The rinse solution supply system 720 has a rinse solution tank 721 that serves as a supply source of the rinse solution such as water, and a flow rate controller (pump) 722 that controls a supply flow rate, and the like of the rinse solution. The gaseous substance supply system 710 and the rinse solution supply system 720 are connected to the anode solution flow path 112a and the cathode gas flow path 122a through pipes. The gaseous substances and rinse solution are supplied to the anode solution flow path 112a and the cathode gas flow path 122a by opening and closing not-illustrated valves. The opening and closing of the valves, and other operations are collectively controlled by the control system 500.

[0080] A part of the reduction products accumulated in the product collection unit 402 is sent to a reduction performance detection unit 501 of the control system 500. In the reduction performance detection unit 501, a production amount and a proportion of each product such as CO or H_2 in the reduction products, are detected. The detected production amount and proportion of each product are input into a data collection and controller 502 of the control system 500. Furthermore, the data collection and controller 502 collects electrical data such as a cell voltage, a cell current, a cathode potential, and an anode potential, and data such as pressure and pressure loss inside the anode solution flow path 112a and the cathode gas flow path 122a as part of cell performance of the electrolysis cell 10, and sends the data to a refresh controller 503.

[0081] The data collection and controller 502 is electrically connected, through bi-directional signal lines whose illustration is partially omitted, to the power supply 20, the pressure controller 101 and the flow rate controller 103 of the anode solution supply system 100, the flow rate controller 302 and the pressure controller 304 of the gas supply system 300, and the pressure controller 712 and the flow rate controller 722 of the refresh material supply 700, in addition to the reduction performance detection unit 501, and these are collectively controlled. Each pipe is provided with a not-illustrated valve, and an opening/closing operation of the valve is controlled by a signal from the data collection and controller 502. The data collection and controller 502 may control operations of the above components during the electrolysis operation, for example.

[0082] The refresh controller 503 is electrically connected, through bi-directional signal lines whose illustration is partially omitted, to the power supply 20, the flow rate controller 103 of the anode solution supply system 100, the flow rate controller 302 of the gas supply system 300, and the pressure controller 712 and flow rate controller 722 of the refresh material supply 700, and these are collectively controlled. Each pipe is provided with a not-illustrated valve, and an opening/closing operation of the valve is controlled by a signal from the refresh controller 503. The refresh controller 503 may control operations of the above components during the electrolysis operation, for example. The refresh controller

503 and the data collection and controller 502 may be configured by a single controller.

[0083] An operating operation of the carbon dioxide electrolysis device 1 of the arrangement will be described. FIG. 9 is a flowchart to explain an operating method example of the carbon dioxide electrolysis device 1. First, as illustrated in FIG. 9, a startup step S101 of the carbon dioxide electrolysis device 1 is performed. In the startup step S101 of the carbon dioxide electrolysis device 1, the following operations are performed. In the anode solution supply system 100, the anode solution is introduced into the anode solution flow path 112a after its flow rate and pressure are controlled by the pressure controller 101 and the flow rate controller 103. In the gas supply system 300, the CO_2 gas is introduced into the cathode gas flow path 122a after its flow rate and pressure are controlled by the flow rate controller 302 and the pressure controller 304.

[0084] Next, a CO_2 electrolysis operation step S102 is performed. In the CO_2 electrolysis operation step S102, application of an electrolysis voltage by the power supply 20 of the electrolysis device 1 that has been subjected to the startup step S101 is started, and a current is supplied by applying a voltage between the anode 111 and the cathode 121. When the current is applied between the anode 111 and the cathode 121, an oxidation reaction near the anode 111 and a reduction reaction near the cathode 121 occur, which will be described below. The explanation of the oxidation and reduction reactions in the first arrangement can be used as appropriate.

[0085] The electrolysis operation may cause salts to precipitate in the cathode gas flow path 122a, resulting in decreased cell performance. This is because ions move between the anode 111 and the cathode 121 through the separator 30 and the ion-exchange membrane, and the ions react with gas components. For example, when a potassium hydroxide solution is used as the anode solution and the carbon dioxide gas is used as the cathode gas, potassium ions move from the anode 111 to the cathode 121 and react with carbon dioxide to produce salts such as potassium hydrogen carbonate and potassium carbonate. When the salts are solubility or less in the cathode gas flow path 122a, the salts precipitate in the cathode gas flow path 122a. The salt precipitation prevents uniform gas flow throughout the cell and decreases the cell performance. The decrease in the cell performance is particularly noticeable when a plurality of cathode gas flow paths 122a are provided. In some cases, the performance of the cell itself can be improved by partially increasing a gas flow rate. This is because the cell performance is improved by increasing a gas pressure, which increases gas components and the like supplied to a catalyst, or by increasing gas diffusibility. A step S103 that determines whether the cell performance meets request criteria is performed to detect such a decrease in the cell performance.

[0086] As mentioned above, the data collection and controller 502 periodically or continuously collects, for example, the production amount and the proportion of each product, the cell performance such as the cell voltage, the cell current, the cathode potential, and the anode potential of the electrolysis cell 10, the pressure inside the anode solution flow path 112a, the pressure inside the cathode gas flow path 122a, and the like. In addition, the data collection and controller 502 has predetermined request criteria for the cell performance, and it is determined whether the collected data meets the set request criteria. When the collected data meets the set request criteria, the CO_2 electrolysis operation is continued without stopping the CO_2 electrolysis (SI04). When the collected data does not meet the set request criteria, a refresh operation step S105 is performed.

[0087] The cell performance collected by the data collection and controller 502 is defined by parameters such as, for example, an upper limit value of the cell voltage when a constant current is applied to the electrolysis cell 10, a lower limit value of the cell current when a constant voltage is applied to the electrolysis cell 10, and Faradaic efficiency of the carbon compounds produced by the reduction reaction of CO_2. Here, the Faradaic efficiency is defined as a proportion of a current that contributed to the production of the desired carbon compound to a total current that flowed in the electrolysis cell 10. To maintain the electrolysis efficiency, it is recommended that the refresh operation step S105 be performed when the upper limit value of the cell voltage reaches 150% or more, preferably 120% or more of the set value when the constant current is applied. The refresh operation step S105 may be performed when the lower limit value of the cell current when the constant voltage is applied reaches 50% or less, preferably 80% or less, of the set value. To maintain the production amount of the reduction products such as the carbon compounds, it is recommended that the refresh operation step S105 be performed when the Faradaic efficiency of the carbon compounds reaches 50% or less, preferably 80% or less, of the set value.

[0088] The cell performance is determined as not meeting the request criteria when at least one of the following parameters, for example, the cell voltage, the cell current, the Faradaic efficiency of the carbon compounds, the pressure inside the anode solution flow path 112a, and the pressure inside the cathode gas flow path 122a, does not meet the request criteria, and the refresh operation step S105 is performed. Two or more of the above parameters may be combined to set the request criteria for the cell performance. For example, the refresh operation step S105 may be performed when both the cell voltage and the Faradaic efficiency of the carbon compounds do not meet the request criteria. The refresh operation step S105 is performed when at least one of the cell performances does not meet the request criteria. The refresh operation step S105 is preferably performed at intervals of, for example, one hour or more to stably perform the CO_2 electrolysis operation step S102.

[0089] When the electrolysis cell 10 mainly produces CO, for example, it can be determined that the request criteria of the cell performance are not met when hydrogen increases to at least 2 times, preferably 1.5 times or more of a normal level. For example, in the case of CO, it can be determined that the request criteria of the cell performance are not met when CO decreases to at least 0.8 times or less, preferably 0.9 times or less, of a normal level.

[0090] When salts are detected, the salts are discharged by the rinse solution. However, when a mass transfer amount does not change even after the salts are discharged, it may be determined that a leak has occurred in the electrolysis cell 10. The leak in the electrolysis cell 10 is not limited to a gas leak between the anode 111 and the cathode 121, but includes, for example, a gas leak from between the cathode 121 and the cathode gas flow path 122a. This gas leak is likely to occur, for example, when the electrolysis cell 10 with salt precipitated is operated for a long time under conditions of high pressure in the cathode gas flow path 122a.

[0091] FIG. 10 is a flowchart to explain an operation example of the refresh operation step S105. First, the application of the electrolysis voltage by the power supply 20 is stopped to stop the reduction reaction of CO_2 (S201). At this time, the application of the electrolysis voltage does not necessarily have to be stopped. Next, the supply of the gas to the cathode gas flow path 122a is stopped, the supply of the anode solution to the anode solution flow path 112a is stopped, and the anode solution is discharged from the anode solution flow path 112a (S202). Next, the rinse solution is supplied (S203) to the anode solution flow path 112a and the cathode gas flow path 122a for cleaning.

[0092] A refresh voltage may be applied between the anode 111 and the cathode 121 while the rinse solution is being supplied. This can remove ions and impurities attached to the cathode catalyst layer. When the refresh voltage is applied so that the process is mainly an oxidation process, ions, impurities such as organic matters on a catalyst surface are oxidized and removed. In addition to refreshing the catalyst, ions substituted in an ion exchange resin when the ion-exchange membrane is used as the separator 30 can be removed by performing this process in the rinse solution.

[0093] The refresh voltage is preferably -2.5 V or more and 2.5 V or less, for example. Since energy is used for the refresh operation, the refresh voltage range is preferably as narrow as possible, and more preferably between -1.5 V or more and 1.5 V or less, for example. The refresh voltage may be applied cyclically so that the oxidation process and the reduction process of ions and impurities are alternately performed. This can accelerate a regeneration of the ion exchange resin and the catalyst. A voltage of a value equivalent to the electrolysis voltage during the electrolysis operation may be applied as the refresh voltage to perform the refresh operation. In this case, a configuration of the power supply 20 can be simplified.

[0094] Next, the gas is supplied to the anode solution flow path 112a and the cathode gas flow path 122a (S204) to dry the cathode 121 and the anode 111. Supplying the rinse solution to the anode solution flow path 112a and the cathode gas flow path 122a increases a water saturation level in the gas diffusion layer and causes a decrease in output due to gas diffusibility. By supplying the gas, the water saturation level is lowered, thus recovering the cell performance and increasing a refreshing effect. The gas is preferably supplied immediately after the distribution of the rinse solution, or at least within 5 minutes after the end of the rinse solution supply. This is because the decrease in the output due to the increase in the water saturation level is significant. For example, when the refresh operation is performed every hour, the output during a 5-minute refresh operation may be 0 V or significantly less, resulting in a loss of 5/60 of the output.

[0095] After the refresh operation is completed, the anode solution is introduced into the anode solution flow path 112a and the CO_2 gas is introduced into the cathode gas flow path 122a (S205). Then, the application of the electrolysis voltage between the anode 111 and the cathode 121 by the power supply 20 is resumed to restart the CO_2 electrolysis operation (S206). When the application of the electrolysis voltage has not been stopped in S201, the restart operation is not performed. The gas may be used, or the rinse solution may be used to discharge the anode solution from the anode solution flow path 112a.

[0096] The supply and flow of the rinse solution (S203) are performed to prevent precipitation of electrolytes contained in the anode solution and to clean the cathode 121, the anode 111, the anode solution flow path 112a, and the cathode gas flow path 122a. Therefore, water is preferable as the rinse solution, further, water with the electrical conductivity of 1 mS/m or less is more preferable, and water with an electrical conductivity of 0.1 mS/m or less is even more preferable. An acid rinse solution such as low-concentration sulfuric acid, nitric acid, hydrochloric acid may be supplied to remove the electrolytes and other precipitates at the cathode 121 and the anode 111, and the like, and the electrolytes may be thereby dissolved. When the low-concentration acid rinse solution is used, a step of supplying a water rinse solution is performed in a subsequent step. Immediately before the gas supply step, the water rinse solution supply step is preferably performed to prevent additives contained in the rinse solution from remaining. FIG. 8 illustrates the rinse solution supply system 720 having one rinse solution tank 721, but when a plurality of rinse solutions are used, such as the water and acid rinse solutions, a plurality of rinse solution tanks 721 are used accordingly.

[0097] An acid or alkaline rinse solution is particularly desirable for refreshing the ion exchange resin. This has the effect of discharging cations and anions that have been substituted for protons and OH^- in the ion exchange resin. For this reason, it is preferable to alternately distribute the acid and alkaline rinse solutions, to combine the rinse solution with water having the electrical conductivity of 1 mS/m or less, and to supply the gas in between the supply of the plurality of rinse solutions to prevent mixing of the rinse solutions.

[0098] The gas used for the gas supply and flow step S204 preferably contains at least one of air, carbon dioxide, oxygen, nitrogen, and argon. Furthermore, it is preferable to use the gas with low chemical reactivity. In this regard, air, nitrogen, and argon are preferably used. Nitrogen and argon are even more preferable. The rinse solution and gas for refreshing is not limited to be supplied to only the anode solution flow path 112a and the cathode gas flow path 122a, but also to the cathode gas flow path 122a to clean a surface of the cathode 121 in contact with the cathode gas flow path 122a. It is effective to supply the gas to the cathode gas flow path 122a to dry the cathode 121 from the surface side in contact with the cathode gas flow path 122a as well.

[0099] The above describes the case where the rinse solution and gas for refreshing are supplied to both the anode part 11 and the cathode part 12, but the rinse solution and gas for refreshing can be supplied to the cathode part 12 only.

[0100] As mentioned above, it is determined whether the CO_2 electrolysis operation step S102 should be continued or the refresh operation step S105 should be performed in accordance with whether the cell performance of the electrolysis cell 10 meets the request criteria. Supplying the rinse solution and gas for refreshing in the refresh operation step S105 prevents uneven distribution of ions and residual gas near the anode 111 and cathode 121, which are factors in the deterioration of the cell performance, and removes the electrolyte precipitation, and the like in the cathode 121, the anode 111, the anode solution flow path 112a, and the cathode gas flow path 122a. Therefore, the cell performance of the electrolysis cell 10 can be recovered by restarting the CO_2 electrolysis operation step S102 after the refresh operation step S105. The CO_2 electrolysis performance by the electrolysis device 1 can be maintained for a long time by repeating the CO_2 electrolysis operation step S102 and the refresh operation step S105 in accordance with the request criteria of the cell performance.

[0101] As mentioned above, in the carbon dioxide electrolysis device of this arrangement, the refresh operation of the electrolysis cell is performed by temporarily flowing the rinse solution through the flow path when salts precipitate, which can prevent the blockage of the flow path. Therefore, the decrease in the electrolysis efficiency of the carbon dioxide electrolysis device can be prevented.

[0102] When performing the refresh operation, the region 122a1 with the hydrophilic inner wall surface 246 and the region 122a2 with the water-repellent inner wall surface 247 are formed in the cathode gas flow path 122a as illustrated in FIG. 7, which enables the rinse solution to easily bypass the salts and flow through the region 122a2, which is near the salts and therefore the salts are easily dissolved, because the hydrophilic inner wall surface 246 is near the salt even if the salts precipitate. In addition, the rinse solution flows into the region 122a2 until the salts are dissolved and can be supplied to the entire surface of the cathode 121, thus efficiently removing the salts.

EXAMPLES

(Example 1)

[0103] A carbon dioxide electrolysis device was fabricated as follows. Iridium oxide was formed on a surface of titanium mesh as an oxidation catalyst. Carbon paper with a catalyst layer was fabricated by spraying carbon, which supports 10.2% by mass gold on the carbon paper with MPL. A membrane electrode composite (catalyst area 4 cm square) was prepared by laminating this carbon paper and titanium mesh with iridium oxide sandwiched by ion-exchange membranes.

[0104] A cathode gas flow path and an anode solution flow path were formed of titanium and were each a serpentine-shaped flow path containing two parallel-connected flow path parts, with a land width of 0.8 mm, a flow path width W of 1 mm, and a flow path depth h of 3 mm. An aspect ratio was 3, and a fluid mean depth M was 0.38. An electrolysis cell was assembled by sandwiching the membrane electrode composite between the anode solution flow path and the cathode gas flow path.

[0105] A 0.1 M potassium hydrogen carbonate solution was supplied to the anode solution flow path at 10 mL/min as an electrolytic solution. Carbon dioxide gas was supplied to the cathode gas flow path at a flow rate of 320 ccm. A current was passed between the anode and the cathode with a stepwise increase in a current value, and gas generated from a cathode side was collected to measure its flow rate and conversion efficiency of carbon dioxide. The gas generated was sampled and identified and quantified by gas chromatography.

[0106] The current value at this time was measured with an ammeter. A partial current density of carbon monoxide (CO), which is an indicator of the percentage used for carbon monoxide production out of a total current density flowed, was found from a conversion efficiency from carbon dioxide to carbon monoxide. Furthermore, a utilization ratio of carbon dioxide at the cathode was found from the conversion efficiency from carbon dioxide to carbon monoxide and a flow rate of the gas generated from the cathode side. A relationship between the partial current density of carbon monoxide and the utilization ratio of carbon dioxide at the cathode was evaluated in accordance with the above.

(Comparative Example 1)

[0107] In the carbon dioxide electrolysis device of Example 1, the electrolysis cell was assembled in the same way as in Example 1, except that the cathode gas flow path was made with the land width of 0.8 mm, the flow path width W of 1 mm, and the flow path depth h of 0.5 mm. The cathode gas flow path had the aspect ratio of 0.5 and the fluid mean depth M of 0.17. The relationship between the partial current density of carbon monoxide and the utilization ratio of carbon dioxide at the cathode was evaluated as in Example 1.

(Comparative Example 2)

[0108] In the carbon dioxide electrolysis device of Example 1, the electrolysis cell was assembled in the same way as in Example 1, except that the cathode gas flow path was made with the land width of 0.8 mm, the flow path width W of 1 mm, and the flow path depth h of 1 mm. The cathode gas flow path had the aspect ratio of 1 and the fluid mean depth of 0.25. The relationship between the partial current density of carbon monoxide and the utilization ratio of carbon dioxide at the cathode was evaluated as in Example 1.

(Comparative Example 3)

[0109] In the carbon dioxide electrolysis device of Example 1, the electrolysis cell was assembled in the same way as in Example 1, except that the cathode gas flow path was made with the land width of 0.8 mm, the flow path width W of 1 mm, and the flow path depth h of 2 mm. The cathode gas flow path had the aspect ratio of 2 and the fluid mean depth of 0.33. The relationship between the partial current density of carbon monoxide and the utilization ratio of carbon dioxide at the cathode was evaluated as in Example 1.

(Comparative Example 4)

[0110] In the carbon dioxide electrolysis device of Example 1, the electrolysis cell was assembled in the same way as in Example 1, except that the cathode gas flow path was made with the land width of 0.49 mm, the flow path width W of 0.49 mm, and the flow path depth h of 1 mm. The cathode gas flow path had the aspect ratio of 2 and the fluid mean depth of 0.16. The relationship between the partial current density of carbon monoxide and the utilization ratio of carbon dioxide at the cathode was evaluated as in Example 1.

[0111] FIG. 11 presents the relationships between the partial current density of carbon monoxide and the utilization ratio of carbon dioxide at the cathode in Example 1, Comparative Example 1, Comparative Example 2, and Comparative Example 3.

[0112] FIG. 12 presents the relationships between the partial current density of carbon monoxide and the utilization ratio of carbon dioxide at the cathode in Comparative Example 3 and Comparative Example 4.

[0113] From FIG. 11, it can be seen that when the aspect ratio of the cathode gas flow path is greater than 1 and 3 or less, and the fluid mean depth M and depth h of the cathode gas flow path satisfy a formula: $h/8 \leq M < h/4$, a high CO_2 utilization ratio of 30% or more can be achieved at a high CO partial current density of 400 mA/cm^2 or more. It can also be seen from FIG. 12 that even if the aspect ratios are the same, the larger the fluid mean depth M is, the higher the CO_2 utilization ratio can be obtained at the high the CO partial current density.

[0114] While certain arrangements have been described, these arrangements have been presented by way of example only, and are not intended to limit the scope of the claims. Indeed, the magnet described herein may be embodied in a variety of other forms; furthermore, various omissions, substitutions and changes in the form of the magnet described herein may be made.

(Numbered Clauses relating to the arrangements)

[0115]

1. A carbon dioxide electrolysis device, comprising:

    a cathode configured to reduce carbon dioxide and thus form a carbon compound;
    an anode configured to oxidize water and thus generate oxygen;
    a cathode gas flow path facing on the cathode and configured to supply gas containing carbon dioxide;
    an anode solution flow path facing on the anode and configured to supply an electrolytic solution containing water; and
    a separator provided between the anode and the cathode, wherein
    an aspect ratio of the cathode gas flow path is greater than 1 and 3 or less, the aspect ratio being defined by a ratio of a depth of the cathode gas flow path to a width of the cathode gas flow path, and
    in a cross-section along a direction perpendicular to a facing surface between the cathode and the cathode gas flow path in the cathode gas flow path, a fluid mean depth M of the cathode gas flow path and a depth h of the cathode gas flow path satisfy a formula: $h/8 \leq M < h/4$, the fluid mean depth M being defined by a ratio of a

circumferential length of the cathode gas flow path to a cross-sectional area of the cathode gas flow path.

2. The device according to clause 1, wherein

the cathode gas flow path includes:
a first region facing on the cathode; and
a second region provided between the first region and an inner bottom surface of the cathode gas flow path, wherein
a width of the second region is wider than a width of the first region.

3. The device according to clause 1, wherein
the cathode gas flow path includes:

a first region facing on the cathode and having a hydrophilic first inner wall surface; and
a second region provided between the first region and an inner bottom surface of the cathode gas flow path and having a water-repellent second inner wall surface.

4. The device according to any one of clauses 1 to 3, wherein
the electrolytic solution contains a metal ion.
5. The device according to any one of clauses 1 to 4, wherein
the cathode contains at least one catalyst selected from the group consisting of copper, gold, and silver.
6. The device according to any one of clauses 1 to 5, further comprising:

an electrolysis cell including the cathode, the anode, the cathode gas flow path, the anode solution flow path, and the separator;
a gas supply configured to supply the gas to the cathode gas flow path;
a solution supply configured to supply the electrolytic solution to the anode solution flow path;
a power supply configured to apply a voltage between the anode and the cathode;
a refresh material supply including a solution supply source configured to supply a rinse solution to the cathode gas flow path; and
a controller configured to control operations of stopping the supply of the gas by the gas supply, stopping the supply of the electrolytic solution by the solution supply, and supplying the rinse solution to the cathode by the refresh material supply in accordance with request criteria of performance of the electrolysis cell.

7. A method of operating a carbon dioxide electrolysis device,

the carbon dioxide electrolysis device including:

a cathode configured to reduce carbon dioxide and thus form a carbon compound;
an anode configured to oxidize water and thus generate oxygen;
a cathode gas flow path facing on the cathode and configured to supply gas containing carbon dioxide;
an anode solution flow path facing on the anode and configured to supply an electrolytic solution containing water; and
a separator provided between the anode and the cathode, wherein
an aspect ratio of the cathode gas flow path is greater than 1 and 3 or less, the aspect ratio being defined by a ratio of a depth of the cathode gas flow path to a width of the cathode gas flow path, and
in a cross-section along a direction perpendicular to a facing surface between the cathode and the cathode gas flow path in the cathode gas flow path, a fluid mean depth M of the cathode gas flow path and a depth h of the cathode gas flow path satisfy a formula: $h/8 \leq M < h/4$, the fluid mean depth M being defined by a ratio of a circumferential length of the cathode gas flow path to a cross-sectional area of the cathode gas flow path,

the method comprising:

supplying gas containing carbon dioxide to the cathode gas flow path and supplying an electrolytic solution to the anode solution flow path;
applying a voltage between the anode and the cathode to reduce carbon dioxide near the cathode of the electrolysis cell to form a carbon compound and to oxidize water or hydroxide ions near the anode to

generate oxygen; and
stopping the supply of the gas and the electrolytic solution and supplying a rinse solution to the cathode gas flow path, in accordance with request criteria of performance of the electrolysis cell.

Claims

1. A carbon dioxide electrolysis device, comprising:

a cathode configured to reduce carbon dioxide and thus form a carbon compound;
an anode configured to oxidize water and thus generate oxygen;
a cathode gas flow path facing on the cathode and configured to supply gas containing carbon dioxide;
an anode solution flow path facing on the anode and configured to supply an electrolytic solution containing water; and
a separator provided between the anode and the cathode, wherein
an aspect ratio of the cathode gas flow path is greater than 1 and 3 or less, the aspect ratio being defined by a ratio of a depth of the cathode gas flow path to a width of the cathode gas flow path, and
in a cross-section along a direction perpendicular to a facing surface between the cathode and the cathode gas flow path in the cathode gas flow path, a fluid mean depth M of the cathode gas flow path and a depth h of the cathode gas flow path satisfy a formula: $h/8 \leq M < h/4$, the fluid mean depth M being defined by a ratio of a circumferential length of the cathode gas flow path to a cross-sectional area of the cathode gas flow path.

2. The device according to claim 1, wherein
the cathode gas flow path includes:

a first region facing on the cathode; and
a second region provided between the first region and an inner bottom surface of the cathode gas flow path, wherein
a width of the second region is wider than a width of the first region.

3. The device according to claim 1, wherein
the cathode gas flow path includes:

a first region facing on the cathode and having a hydrophilic first inner wall surface; and
a second region provided between the first region and an inner bottom surface of the cathode gas flow path and having a water-repellent second inner wall surface.

4. The device according to any one of claims 1 to 3, wherein
the electrolytic solution contains a metal ion.

5. The device according to any one of claims 1 to 4, wherein
the cathode contains at least one catalyst selected from the group consisting of copper, gold, and silver.

6. The device according to any one of claims 1 to 5, further comprising:

an electrolysis cell including the cathode, the anode, the cathode gas flow path, the anode solution flow path, and the separator;
a gas supply configured to supply the gas to the cathode gas flow path;
a solution supply configured to supply the electrolytic solution to the anode solution flow path;
a power supply configured to apply a voltage between the anode and the cathode;
a refresh material supply including a solution supply source configured to supply a rinse solution to the cathode gas flow path; and
a controller configured to control operations of stopping the supply of the gas by the gas supply, stopping the supply of the electrolytic solution by the solution supply, and supplying the rinse solution to the cathode by the refresh material supply in accordance with request criteria of performance of the electrolysis cell.

7. A method of operating a carbon dioxide electrolysis device, the carbon dioxide electrolysis device including:

a cathode configured to reduce carbon dioxide and thus form a carbon compound;
an anode configured to oxidize water and thus generate oxygen;
a cathode gas flow path facing on the cathode and configured to supply gas containing carbon dioxide;
an anode solution flow path facing on the anode and configured to supply an electrolytic solution containing water; and
a separator provided between the anode and the cathode, wherein
an aspect ratio of the cathode gas flow path is greater than 1 and 3 or less, the aspect ratio being defined by a ratio of a depth of the cathode gas flow path to a width of the cathode gas flow path, and
in a cross-section along a direction perpendicular to a facing surface between the cathode and the cathode gas flow path in the cathode gas flow path, a fluid mean depth M of the cathode gas flow path and a depth h of the cathode gas flow path satisfy a formula: $h/8 \leq M < h/4$, the fluid mean depth M being defined by a ratio of a circumferential length of the cathode gas flow path to a cross-sectional area of the cathode gas flow path,

the method comprising:

supplying gas containing carbon dioxide to the cathode gas flow path and supplying an electrolytic solution to the anode solution flow path;
applying a voltage between the anode and the cathode to reduce carbon dioxide near the cathode of the electrolysis cell to form a carbon compound and to oxidize water or hydroxide ions near the anode to generate oxygen; and
stopping the supply of the gas and the electrolytic solution and supplying a rinse solution to the cathode gas flow path, in accordance with request criteria of performance of the electrolysis cell.

FIG. 1

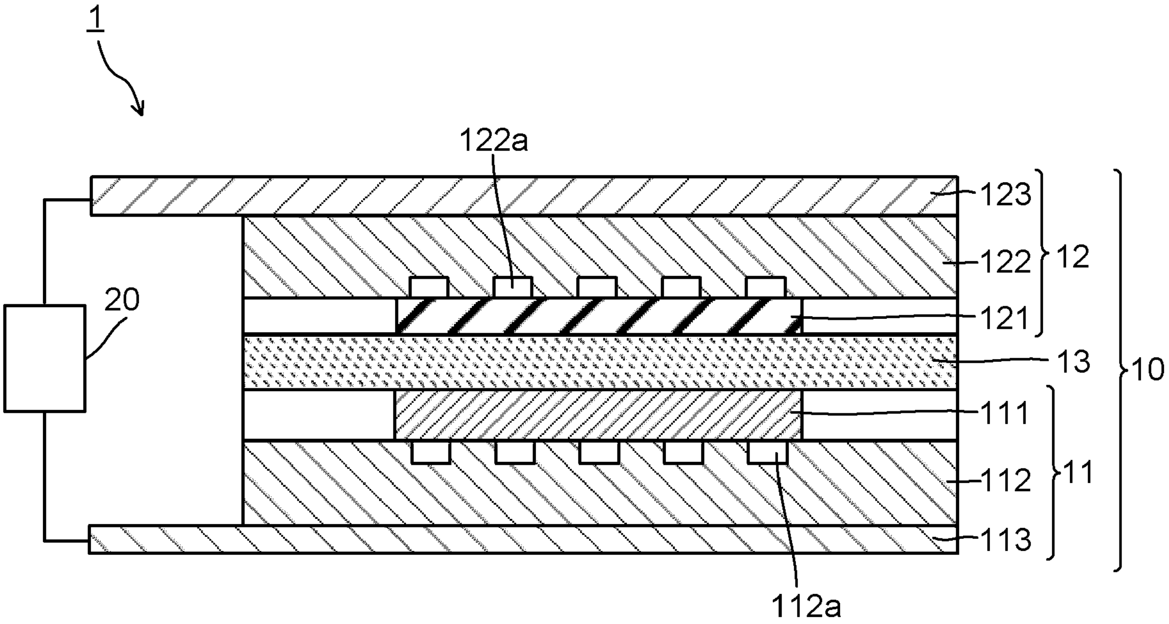


FIG. 2

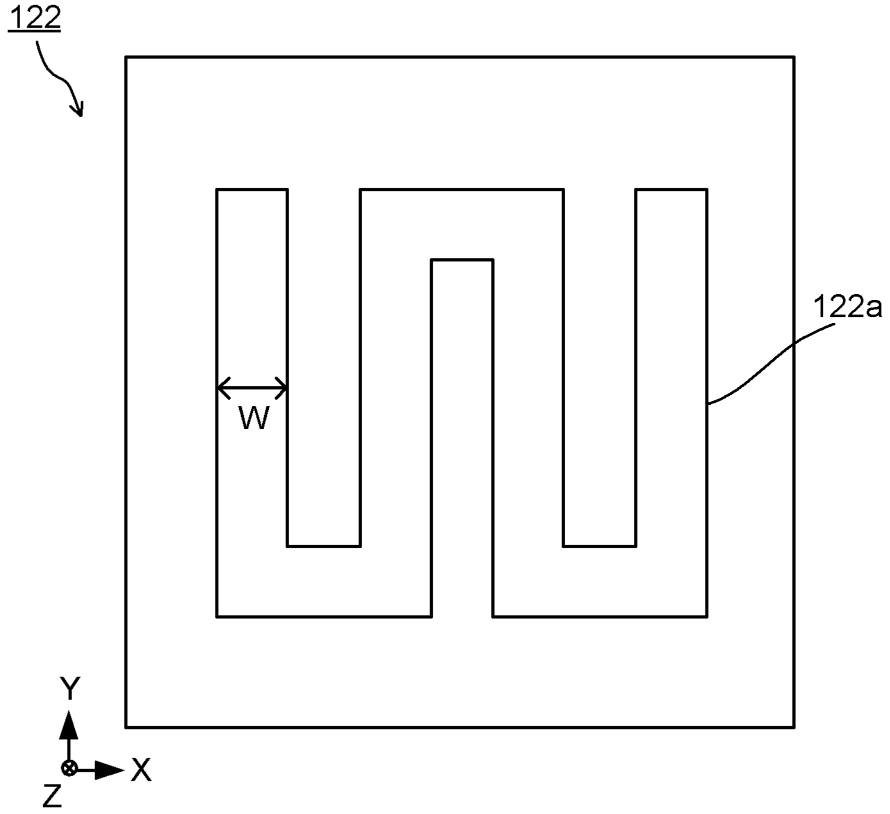


FIG. 3

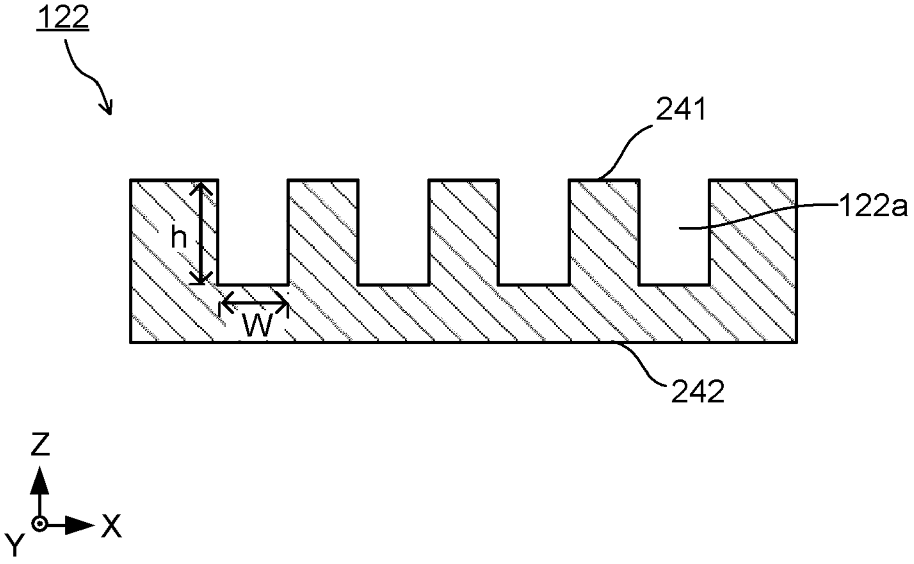


FIG. 4

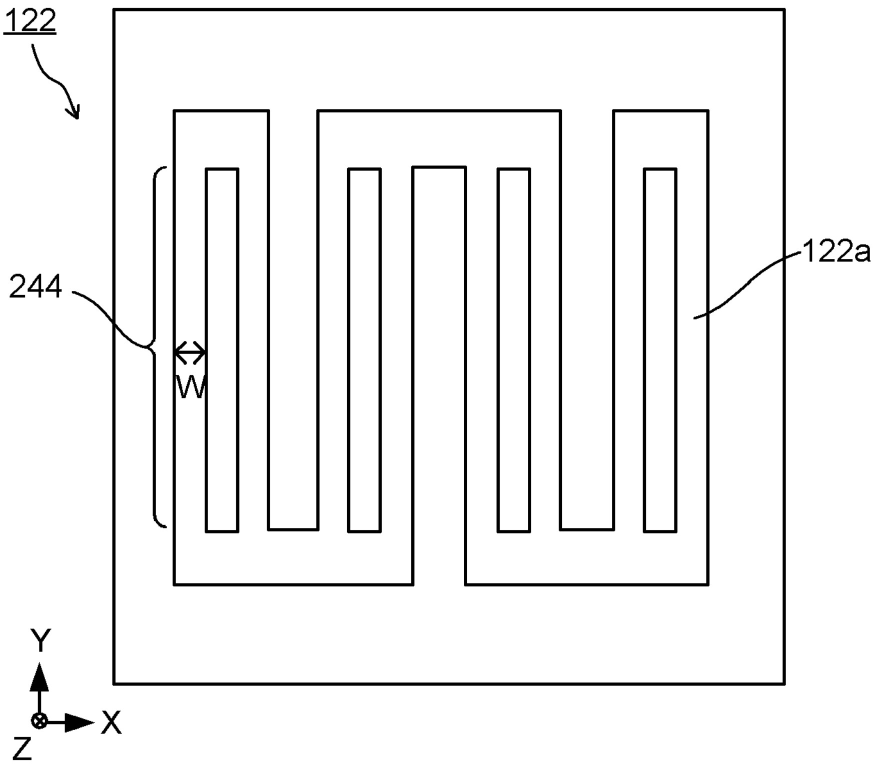


FIG. 5

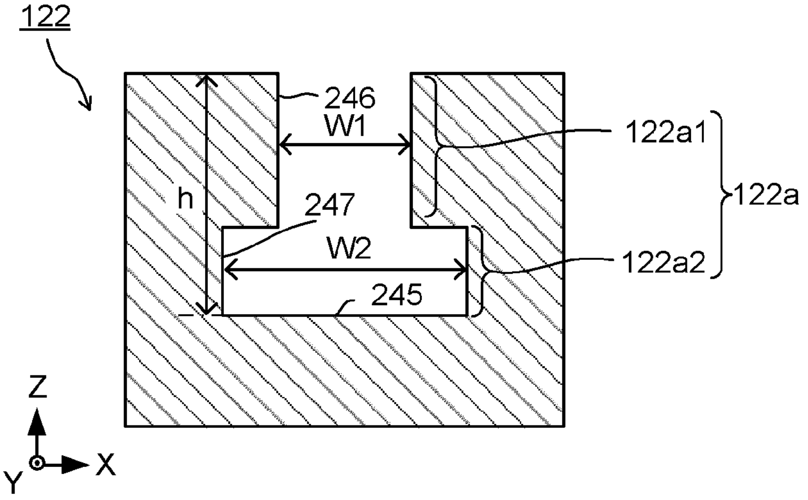


FIG. 6

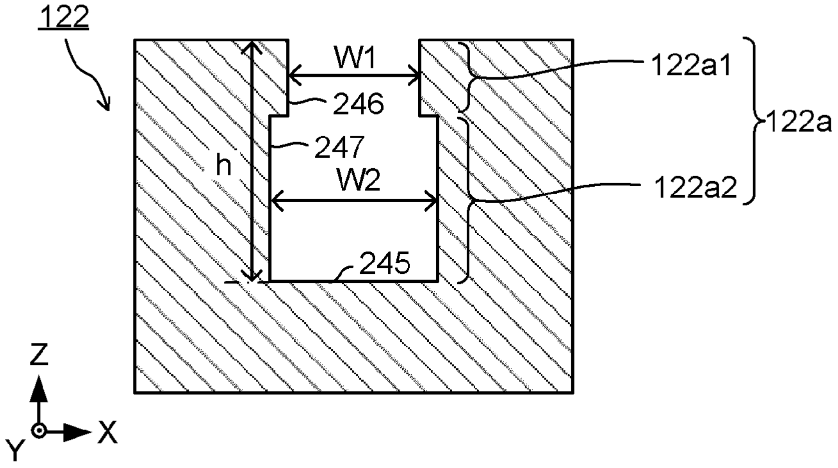


FIG. 7

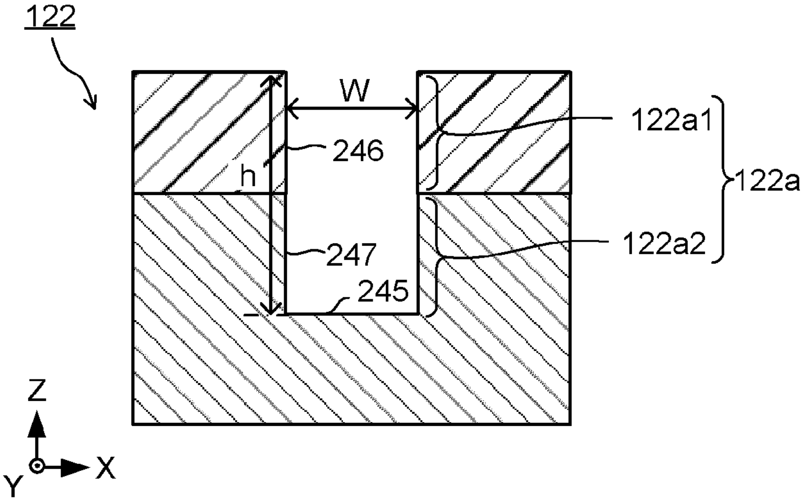
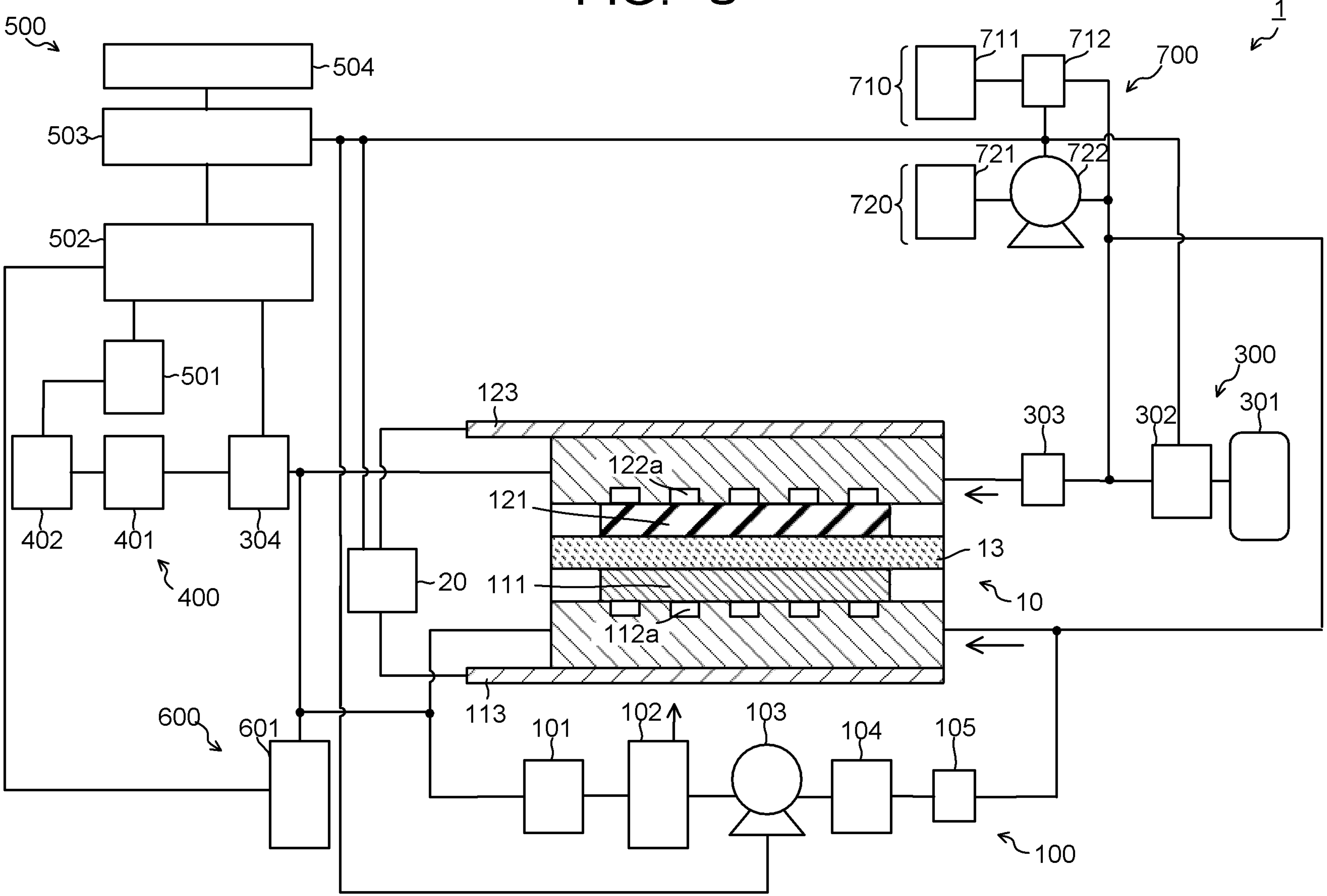


FIG. 8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103
104
105
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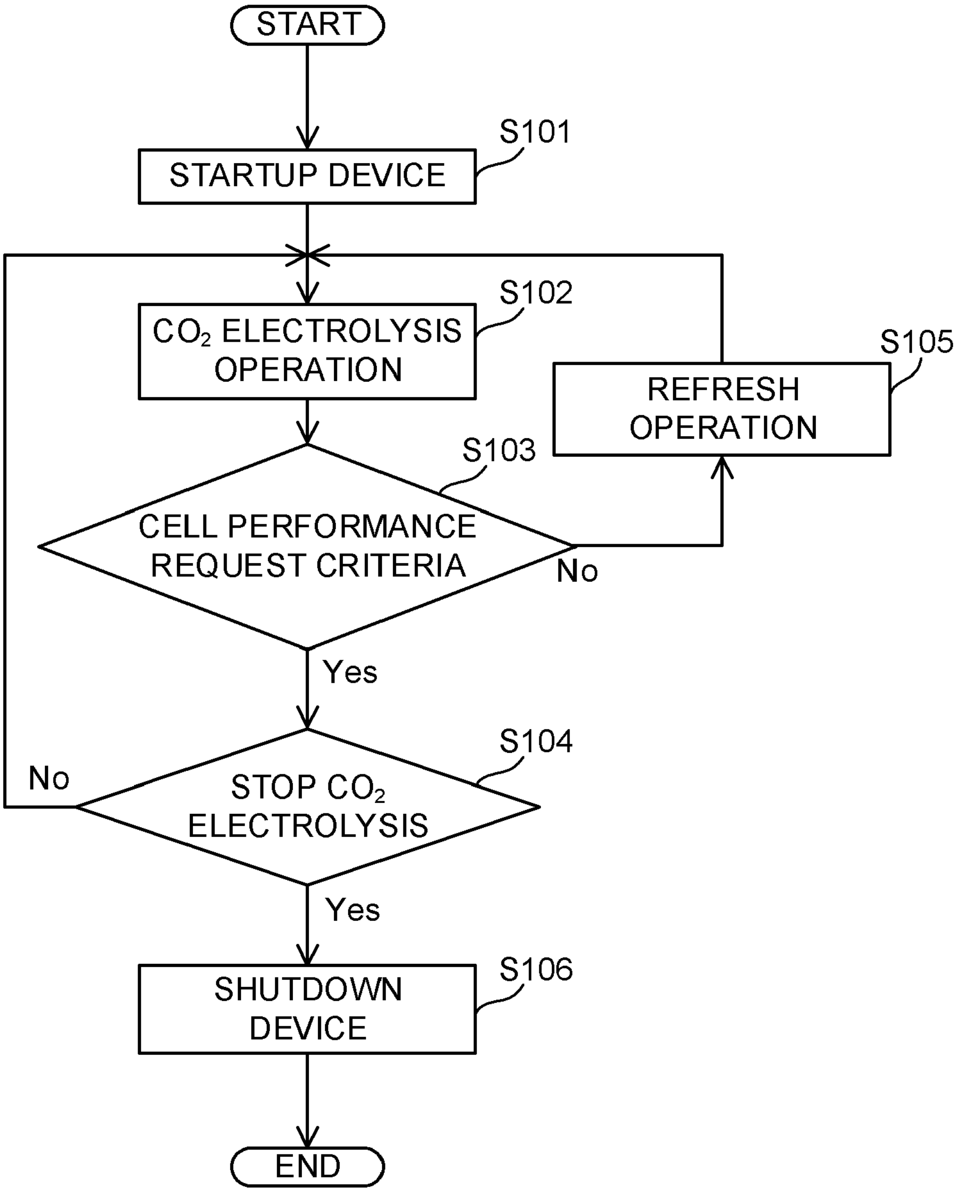
FIG. 9


START
STARTUP DEVICE
S101
CO2 ELECTROLYSIS OPERATION
S102
CELL PERFORMANCE REQUEST CRITERIA
S103
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REFRESH OPERATION
S105
Yes
STOP CO2 ELECTROLYSIS
S104
No
Yes
SHUTDOWN DEVICE
S106
END

FIG. 10

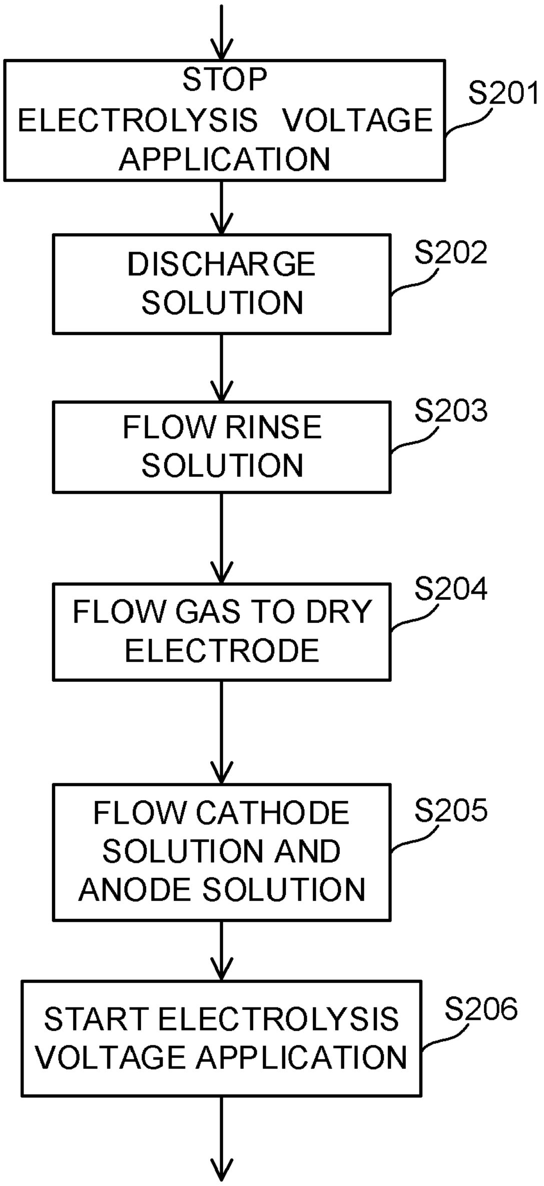
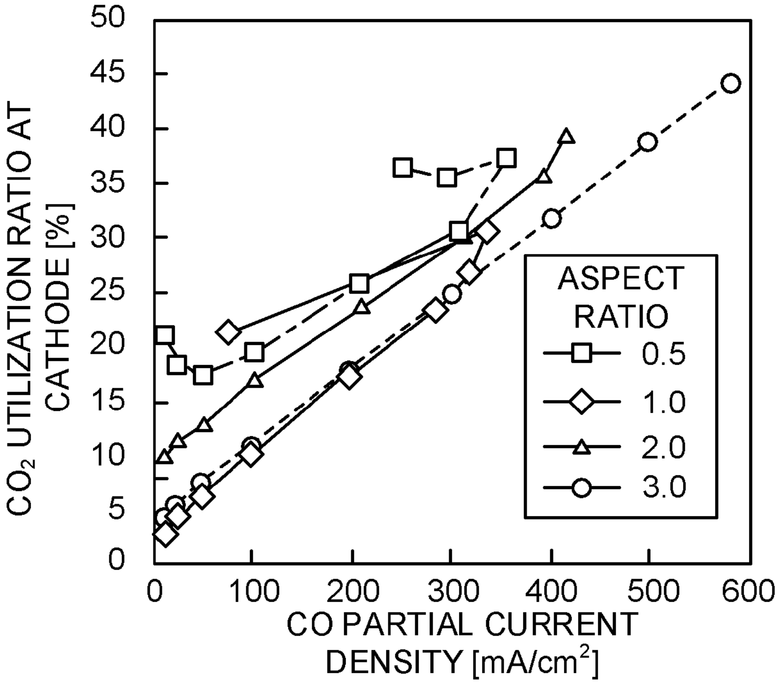

STOP ELECTROLYSIS VOLTAGE APPLICATION
S201
DISCHARGE SOLUTION
S202
FLOW RINSE SOLUTION
S203
FLOW GAS TO DRY ELECTRODE
S204
FLOW CATHODE SOLUTION AND ANODE SOLUTION
S205
START ELECTROLYSIS VOLTAGE APPLICATION
S206

FIG. 11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300
400
500
600
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ASPECT RATIO
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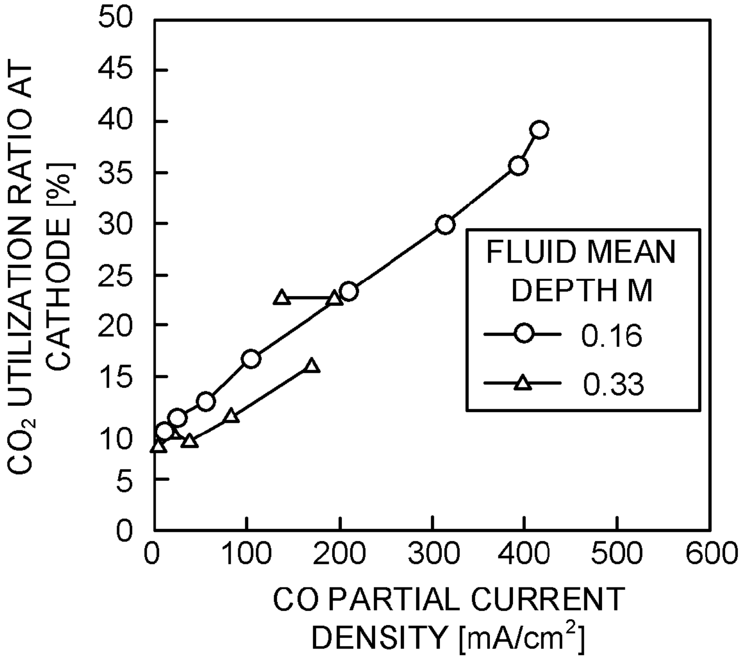
1.0
2.0
3.0

FIG. 12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400
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CO PARTIAL CURRENT DENSITY [mA/cm^2]
FLUID MEAN DEPTH M
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0.33

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EUROPEAN SEARCH REPORT

Application Number
EP 21 19 3516

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 3 378 969 A1 (TOSHIBA KK [JP]) 26 September 2018 (2018-09-26) * the whole document * -----	1-7	INV. C25B1/50 C25B3/26 C25B9/19 C25B9/60 C25B15/08
A	EP 3 623 501 A1 (TOSHIBA KK [JP]) 18 March 2020 (2020-03-18) * the whole document * -----	1-7	
A	WO 2020/240218 A1 (UNIV SZEGEDI [HU]; THALESNANO ZRT [HU]) 3 December 2020 (2020-12-03) * the whole document * -----	1-7	
			TECHNICAL FIELDS SEARCHED (IPC)
			C25B

1 The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	17 February 2022	Juhart, Matjaz

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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D : document cited in the application
L : document cited for other reasons
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& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 21 19 3516

17-02-2022

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