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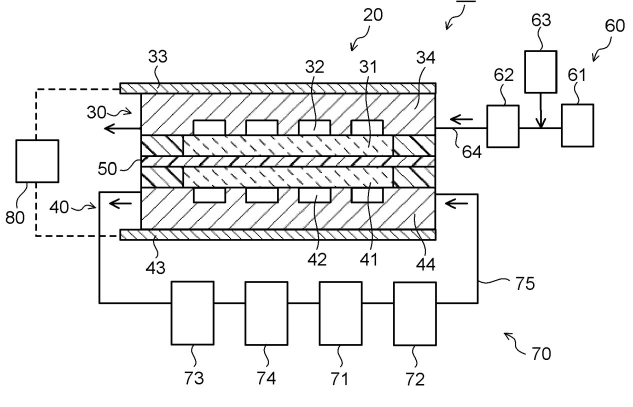
(54) CARBON DIOXIDE ELECTROLYTIC DEVICE AND METHOD OF ELECTROLYZING CARBON DIOXIDE

(57) A carbon dioxide electrolytic device of an embodiment includes: an electrolysis cell including a cathode to reduce carbon dioxide, an anode to oxidize water or hydroxide ion and having a base containing titanium, a cathode flow path to supply carbon dioxide to the cathode, an anode flow path to supply an electrolytic solution containing water to the anode, and a separator to separate the anode and the cathode; a gas supply unit to supply carbon dioxide to the cathode flow path; at least either of a humidifier to humidify carbon dioxide supplied to the cathode flow path by using a humidification water, and a liquid pouring part to add the humidification water to the carbon dioxide; and an electrolytic solution supply unit to supply the electrolytic solution to the anode flow path. At least one of the electrolytic solution, the humidification water, and the supplied gas contains an oxidant.

FIG. 1



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Description

FIELD

[0001] Arrangements disclosed herein relate to a carbon dioxide electrolytic device and a method of electrolyzing carbon dioxide.

BACKGROUND

[0002] In recent years, from both viewpoints of energy problems and environmental problems, it is desired not only to convert renewable energy such as sunlight into electric energy and use it but also to convert it into a storable and transportable state. In response to such a desire, research and development of Power to Chemicals technology of producing chemical substances using sunlight such as photosynthesis by plants are in progress. Such technology allows the renewable energy to be stored as storable fuel or the like, and it is expected to create value by producing chemical substances serving as industrial raw materials.

[0003] As devices that produce the chemical substances using the renewable energy such as sunlight, for example, there is known an electrolytic device that reduces carbon dioxide (CO_2) generated from a power plant, an incinerator, or the like. A CO_2 electrolytic device includes a cathode (reduction electrode) that reduces CO_2 to produce a carbon compound such as carbon monoxide (CO), and an anode (oxidation electrode) that oxidizes water (H_2O) or hydroxide ions (OH^-). It is effective to apply, to such a CO_2 electrolytic device, a cell structure (electrolysis cell) in which the cathode and the anode are stacked with a separator such as an ion exchange membrane or a porous membrane interposed therebetween, and direct supply of CO_2 to a cathode catalyst layer of the electrolysis cell allows a reduction reaction of CO_2 to rapidly progress.

[0004] In the aforementioned electrolysis cell, in order to improve its durability, prevention of a change (deterioration) in composing members of the electrolysis cell is demanded. For example, a porous base of the anode (oxidation electrode) uses titanium (Ti) as a material having low chemical reactivity and high conductivity. Although Ti is known as a material having low chemical reactivity and excellent corrosion resistance, it is being clarified that if an operation is continued for a long period of time in a state of being in contact with an alkaline electrolytic solution, elution occurs in the porous base made of Ti, which causes pore clogging or the like in the porous base. Accordingly, it is being required to prevent the elution and the like of the porous base made of Ti caused by the electrolytic solution.

SUMMARY

[0005] A subject be solved by the aspect of the present invention is to provide a carbon dioxide electrolytic device and a method of electrolyzing carbon dioxide capable of preventing a characteristic deterioration and the like of an electrolysis cell by preventing elution and the like of an anode.

[0006] According to the aspects of the present invention, there is provided a carbon dioxide electrolytic device and a method of electrolyzing carbon dioxide capable of preventing a characteristic deterioration and the like of an electrolysis cell by preventing elution and the like of an anode.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007]

FIG. 1 is a view illustrating a first example of a carbon dioxide electrolytic device of an arrangement.
FIG. 2 is a view illustrating a second example of the carbon dioxide electrolytic device of the arrangement.

DETAILED DESCRIPTION

[0008] A carbon dioxide electrolytic device of an arrangement includes: an electrolysis cell including a cathode configured to reduce carbon dioxide to produce a carbon compound, an anode configured to oxidize water or hydroxide ion to produce oxygen and having a base containing titanium, a cathode flow path configured to supply carbon dioxide to the cathode, an anode flow path configured to supply an electrolytic solution containing water to the anode, and a separator configured to separate the anode and the cathode; a gas supply unit configured to supply carbon dioxide to the cathode flow path; at least one of a humidifier configured to humidify carbon dioxide supplied to the cathode flow path by using a humidification water, and a liquid pouring part configured to add the humidification water to the carbon dioxide; and an electrolytic solution supply unit configured to supply the electrolytic solution to the anode flow path. In the carbon dioxide electrolytic device of the arrangement, at least one of the electrolytic solution and the humidification water contains an oxidant; and/or the carbon dioxide gas supplied to the cathode flow path contains at least one selected from a group consisting of nitrogen dioxide, nitrogen monoxide, and ozone.

[0009] Hereinafter, a carbon dioxide electrolytic device and a method of electrolyzing carbon dioxide of arrangements will be explained with reference to the drawings. Note that in respective arrangements, substantially the same components are denoted by the same reference numerals, and explanation thereof is sometimes partially omitted. The drawings are schematic, and the relation of thickness and planer dimension of the respective parts, a thickness ratio of the respective parts, and so on may be different from actual ones.

[0010] A carbon dioxide electrolytic device of an arrangement will be explained with reference to FIG. 1 and FIG. 2. FIG. 1 is a sectional view illustrating a first example of a carbon dioxide (CO_2) electrolytic device 10 of the arrangement. FIG. 2 is a sectional view illustrating a second example of the carbon dioxide (CO_2) electrolytic device 10 of the arrangement. The CO_2 electrolytic device 10 illustrated in FIG. 1 and FIG. 2 includes an electrolysis cell 20. The electrolysis cell 20 includes a cathode part 30, an anode part 40, and a separator 50 disposed to separate these.

[0011] The cathode part 30 includes a reduction electrode (cathode) 31 having a metal catalyst layer, a cathode flow path 32, and a cathode current collector 33. The cathode flow path 32 is a gas flow path that supplies a CO_2 gas to the cathode 31, and is formed of a pit (groove) provided in a cathode flow path plate 34. The cathode 31 is disposed to be in contact with CO_2 flowing through the cathode flow path 32. The anode part 40 includes an anode (oxidation electrode) 41, an anode flow path 42, and an anode current collector 43. The anode flow path 42 is an electrolytic solution flow path that supplies an electrolytic solution as an anode solution to the anode 41, and is formed of a pit (groove) provided in an anode flow path plate 44. The anode 41 is disposed to be in contact with the anode solution flowing through the anode flow path 42.

[0012] The CO_2 electrolytic device 10 includes a gas supply unit 60 that supplies CO_2 to the electrolysis cell 20, and an anode solution supply unit (supply system) 70 that supplies the anode solution to the electrolysis cell 20. The gas supply unit 60 includes a CO_2 storage part 61 such as a CO_2 gas cylinder, a humidification water supply part that supplies a humidification water to the CO_2 gas, and a gas addition part 63 that adds an additive gas to the CO_2 gas. The electrolytic device 10 illustrated in FIG. 1 includes a humidification part 62 that humidifies the CO_2 gas, as the humidification water supply part. The electrolytic device 10 illustrated in FIG. 2 includes a liquid pouring part (liquid pouring pipe) 65 that adds the humidification water to the CO_2 gas, as the humidification water supply part. The gas supply unit 60 supplies the humidified CO_2 gas to the cathode flow path 32 via a gas pipe 64.

[0013] The CO_2 gas supplied to the cathode flow path 32 is not limited to a single gas of CO_2, and may also be gas mainly composed of CO_2 (for example, gas containing CO_2 of 90 vol% or more). In the cathode 31 of the electrolysis cell 20 illustrated in FIG. 1 and FIG. 2, ions are supplied via the separator 50, and the CO_2 gas is supplied from the cathode flow path 32. A CO_2 reduction product is discharged mainly from the cathode flow path 32.

[0014] The electrolytic solution supply unit 70 includes an anode solution tank 71, a pump 72, an anode solution concentration measurement part 73, and an oxidant supply part 74, and supplies the anode solution to the anode flow path 42 from the anode solution tank 71 via the pump 72 and an electrolytic solution pipe 75. The anode solution circulates through the anode flow path 42 and the electrolytic solution pipe 75. The cathode current collector 33 and the anode current collector 43 in the CO_2 electrolytic device 10 are connected to a power supply 80. For the anode flow path plate 44 forming the anode flow path 42, and the cathode flow path plate 34 forming the cathode flow path 32, a material having low chemical reactivity and having high conductivity is preferably used. As such a material, there can be cited a metal material such as Ti or SUS, carbon, or the like.

[0015] Generally, the electrolysis cell 20 is sandwiched by a pair of support plates (not illustrated), and further tightened by bolts or the like. The power supply 80 connected to the cathode current collector 33 and the anode current collector 43 is not limited to an ordinary commercial power supply, a battery, or the like, and may be a power supply that converts renewable energy into electric energy and supplies it. As examples of such a power supply, there can be cited a power supply that converts kinetic energy or potential energy such as wind power, water power, geothermal power or tidal power into electric energy, a power supply like a solar cell such as a photoelectric conversion element that converts light energy into electric energy, a power supply such as a fuel cell or a storage battery that converts chemical energy into electric energy, and a power supply such as a device that converts vibrational energy such as sound into electric energy. The use of renewable energy is preferable in terms of the environment since it also enables effective use of carbon dioxide.

[0016] The cathode 31 is an electrode (reduction electrode) that causes a reduction reaction of carbon dioxide (CO_2) to produce a carbon compound such as carbon monoxide (CO), methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), methanol (CH_3OH), ethanol (C_2H_5OH), or ethylene glycol ($C_2H_6O_2$). In the cathode 31, a side reaction in which hydrogen (H_2) is produced by a reduction reaction of water (H_2O) is sometimes caused simultaneously with the reduction reaction of carbon dioxide (CO_2). The cathode 31 has a first surface in contact with the separator 50, and a second surface facing the cathode flow path 32. The first surface of the cathode 31 is in contact with one surface of the separator 50.

[0017] The cathode flow path 32 being a flow path of the gas containing CO_2 (hereinafter, also described as a CO_2 gas) is formed of a pit (groove portion/recessed portion) provided in the cathode flow path plate 34. The cathode flow path plate 34 is provided with gas introduction port and discharge port, whose illustration is omitted. The CO_2 gas is introduced from the gas supply unit 60 via the gas introduction port or the gas discharge port. Further, a reaction product gas containing CO, H_2, or the like is discharged via the gas introduction port or the gas discharge port, and the discharged gas is sent to a not-illustrated valuable manufacturing part or collected by a product collecting part. The cathode flow path plate 34 and the cathode flow path 32 provided in the cathode flow path plate 34 are provided to be in contact with the second surface on a side opposite to the first surface that is in contact with the separator 50, of the cathode 31.

[0018] The cathode 31 has a structure capable of making ions and water move between the separator 50 and the cathode flow path 32, for example, a porous structure of a mesh material, a punched material, a porous body, a metal fiber sintered body, or the like. The cathode catalyst material may have nanoparticles, a nanostructure, a nanowire, or the like for the purpose of increasing the reduction reaction. The nanostructure is a structure having nanoscale irregularities on a surface of the catalyst material and the like. The cathode 31 has a porous gas diffusion base and a porous cathode catalyst layer, for example. Between the gas diffusion base and the cathode catalyst layer, a porous layer (gas diffusion layer) denser than the gas diffusion base may be disposed. The gas diffusion base is disposed on the cathode flow path 32 side, and the cathode catalyst layer is disposed on the separator 50 side. The cathode catalyst layer may enter the gas diffusion layer. As described above, the cathode 31 has a porous structure.

[0019] The cathode catalyst layer preferably has catalyst nanoparticles, a catalyst nanostructure, or the like. The gas diffusion base is constituted of, for example, carbon paper, carbon cloth, or the like, and is preferably subjected to water repellent treatment. The cathode catalyst layer is supplied with ions from the anode 41 via the separator 50. In the gas diffusion base, from the cathode flow path 32, the CO_2 gas is supplied and a product obtained by the reduction reaction of the CO_2 gas is discharged. The reduction reaction of CO_2 occurs at a three-phase boundary of the cathode catalyst layer, and a gaseous product is discharged from the cathode flow path 32.

[0020] The cathode catalyst layer of the cathode 31 is preferably constituted of a catalyst material (cathode catalyst material) capable of reducing CO_2 to produce a carbon compound and capable of reducing an overvoltage in the above reaction. As the cathode catalyst material, there can be cited a metal such as gold (Au), silver (Ag), copper (Cu), platinum (Pt), palladium (Pd), nickel (Ni), cobalt (Co), iron (Fe), manganese (Mn), titanium (Ti), cadmium (Cd), zinc (Zn), indium (In), gallium (Ga), lead (Pb), or tin (Sn), a metal material such as an alloy or an intermetallic compound containing at least one of the above metals, a carbon material such as carbon (C), graphene, CNT (carbon nanotube), fullerene, or ketjen black, or a metal complex such as a Ru complex or a Re complex. The cathode catalyst layer can employ various shapes such as a plate shape, a mesh shape, a wire shape, a particle shape, a porous shape, a thin film shape, and an island shape.

[0021] The anode 41 is an electrode (oxidation electrode) that causes an oxidation reaction of water (H_2O) in the anode solution to produce oxygen (O_2) and hydrogen ions (H^+), or causes an oxidation reaction of hydroxide ions (OH^-) produced in the cathode part 30 to produce oxygen and water. The anode 41 is disposed between the separator 50 and the anode flow path 42 to be in contact with them. More specifically, the anode 41 has a first surface in contact with the separator 50, and a second surface facing the anode flow path 42. The first surface of the anode 41 is in close contact with the separator 50. A solution inlet port and a solution outlet port (both of which are not illustrated) are connected to the anode flow path plate 44, and via these solution inlet port and solution outlet port, the anode solution is introduced and discharged by the pump 72. The anode solution flows through the inside of the anode flow path 42 so as to be brought into contact with the anode 41. The anode current collector 43 is in electrical contact with a surface on a side opposite to the anode 41, of the anode flow path plate 44 that forms the anode flow path 42.

[0022] When an aqueous electrolyte solution is used as the anode solution, the anode 41 is preferably composed mainly 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 reducing an overvoltage in the above reaction. As such a catalyst material, there can be cited a metal such as platinum (Pt), palladium (Pd), or nickel (Ni), an alloy or an intermetallic compound containing the above metal, a binary metal oxide such as a manganese oxide (Mn-O), an iridium oxide (Ir-O), a nickel oxide (Ni-O), a cobalt oxide (Co-O), an iron oxide (Fe-O), a tin oxide (Sn-O), an indium oxide (In-O), a ruthenium oxide (Ru-O), a lithium oxide (Li-O), or a lanthanum oxide (La-O), a ternary metal oxide such as Ni-Co-O, Ni-Fe-O, La-Co-O, Ni-La-O, or Sr-Fe-O, a quaternary metal oxide such as Pb-Ru-Ir-O or La-Sr-Co-O, or a metal complex such as a Ru complex or an Fe complex.

[0023] The anode 41 includes a base (porous base) having a structure capable of moving the anode solution and ions between the separator 50 and the anode flow path 42, for example, a porous structure such as a mesh material, a punched material, or a porous sintered body. The porous base is preferably composed of Ti or a Ti alloy having low reactivity. When the oxide is used as the anode catalyst material, it is preferable to form a catalyst layer by attaching or staking the anode catalyst material on the surface of the porous base composed of the metal material containing Ti described above. The anode catalyst material preferably has a shape of a nanoparticle, a nanostructure, a nanowire, or the like in order to enhance the oxidation reaction. The nanostructure is a structure having nanoscale irregularities on the surface of the catalyst material.

[0024] As the anode solution, an aqueous solution containing an arbitrary electrolyte can be used. As the aqueous solution containing the electrolyte, there can be cited, for example, an aqueous solution containing a phosphate ion

(PO_4^{2-}), a borate ion (BO_3^{3-}), a sodium ion (Na^+), a potassium ion (K^+), a calcium ion (Ca^{2+}), a lithium ion (Li^+), a cesium ion (Cs^+), a magnesium ion (Mg^{2+}), a chloride ion (Cl^-), a hydrogen carbonate ion (HCO_3^-), a carbonate ion (CO_3^{2-}), or the like. A pH of the anode solution is not particularly limited, but it is preferably 6 or more and 10 or less when considering use environments. Besides, the anode solution is more preferably an alkaline solution containing HCO_3^-, CO_3^{2-}, $LiHCO_3$, $NaHCO_3$, $KHCO_3$, or the like.

[0025] The separator 50 is composed of a material capable of moving ions between the anode 41 and the cathode 31, and capable of separating the anode part 40 and the cathode part 30, and is formed of, for example, a porous membrane made an organic polymeric material, an ion exchange membrane, or the like. The organic material forming the porous membrane used for the separator 50 is not limited in particular, and examples thereof include a fluorocarbon resin such as Teflon (registered trademark), hydrocarbon polymers such as polyether, polysulfone, polyethylene, and polypropylene, cellulose, and the like. As the ion exchange membrane, there can be cited, for example, a cation exchange membrane such as Nafion (registered trademark) or Flemion (registered trademark), or an anion exchange membrane such as Neosepta (registered trademark), Selemion (registered trademark), Sustainion (registered trademark), or PiperION (registered trademark).

[0026] The supplied CO_2 gas may be supplied in a dry state, but is more preferably humidified. This can prevent drying of the membrane when the ion exchange membrane is used for the separator 50. Further, when the porous membrane made of the organic polymeric material is used for the separator 50, by using a CO_2 gas in a humidified state, a wet seal is formed on the porous membrane made of the organic polymeric material. Such a wet seal can prevent a crossover between the anode part 40 and the cathode part 30, namely, a to-and-fro movement of gas and liquid between the anode part 40 and the cathode part 30 and a reaction of mutual gasses caused by the movement.

[0027] In order to humidify the CO_2 gas, it is possible that a humidification part is provided and the gas is humidified by making water vapor to be contained in the gas, a liquid pouring part for humidification is provided and the gas is humidified by pouring water in the gas, or a rinse solution is introduced into the gas on a regular basis. For example, in FIG. 1, the gas supply unit 60 includes the humidification part 62 that humidifies the CO_2 gas flowing through the gas pipe 64. The humidification part (humidification device) 62 includes a humidification water tank, for example, and is configured to humidify the CO_2 gas by vaporizing the humidification water by using an ultrasonic oscillator or the like. Further, it is also possible to humidify the CO_2 gas by making the CO_2 gas to be bubbled and passed through the inside of the humidification water tank. In FIG. 2, the gas supply unit 60 includes the liquid pouring part (liquid pouring pipe) 65 that adds the humidification water to the CO_2 gas flowing through the gas pipe 64.

[0028] Next, an operation of the carbon dioxide electrolytic device 10 illustrated in FIG. 1 and FIG. 2 will be described. Here, a case of producing carbon monoxide (CO) as the carbon compound is mainly explained. However, the carbon compound as the reduction product of carbon dioxide is not limited to carbon monoxide, and may be methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), methanol (CH_3OH), ethanol (C_2H_5OH), ethylene glycol ($C_2H_6O_2$), or the like, and furthermore, carbon monoxide being a reduction product may be further reduced to produce the organic compounds described above.

[0029] First, the reaction process when water (H_2O) is oxidized mainly to produce hydrogen ions (H^+) is described. When a current is supplied from the power supply 80 between the anode 41 and the cathode 31, an oxidation reaction of water (H_2O) occurs in the anode 41 that is in contact with the anode solution. Concretely, as presented in the following formula (1), H_2O contained in the anode solution is oxidized, and oxygen (O_2) and hydrogen ions (H^+) are produced.

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

[0030] H^+ produced in the anode moves in the electrolytic solution that exists in the anode 41 and the separator 50, and reaches the vicinity of the cathode 31. The reduction reaction of carbon dioxide (CO_2) is caused by electrons (e^-) based on the current supplied from the power supply 80 to the cathode 31 and H^+ moved to the vicinity of the cathode 31. Concretely, as presented in the following formula (2), CO_2 supplied from the cathode flow path 32 to the cathode 31 is reduced to produce CO. Further, as presented in the following formula (3), hydrogen ions (H^+) receive electrons, thereby producing hydrogen. At this time, hydrogen may be produced simultaneously with carbon monoxide.

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

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

[0031] Next, the reaction process when carbon dioxide (CO_2) is reduced mainly to produce hydroxide ions (OH^-) is described. When a current is supplied from the power supply 80 between the anode 41 and the cathode 31, in the vicinity of the cathode 31, water (H_2O) and carbon dioxide (CO_2) are reduced to produce carbon monoxide (CO) and hydroxide ions (OH^-), as presented in the following formula (4). Further, as presented in the following formula (5), water receives electrons, thereby producing hydrogen. At this time, hydrogen may be produced simultaneously with carbon monoxide.

The hydroxide ions (OH^-) produced by these reactions diffuse in the vicinity of the anode 41, and as presented in the following formula (6), the hydroxide ions (OH^-) are oxidized to produce oxygen (O_2).

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

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

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

[0032] Such a carbon dioxide electrolytic device 10 of the arrangement is not specialized in only the reduction of carbon dioxide, but it can produce carbon monoxide and hydrogen at 1:2, and produce a carbon dioxide reduction product and hydrogen at such an arbitrary ratio as to produce methanol in a chemical reaction thereafter, for example. Hydrogen is a material that is inexpensive and easy to obtain through the electrolysis of water and from fossil fuel, so that a ratio of hydrogen is not required to be large. From these viewpoints, it is preferable that a ratio of carbon monoxide to hydrogen is at least 1 or more, and desirably 1.5 or more, in terms of economical and environmental viewpoints.

[0033] In the carbon dioxide electrolytic device 10 of the arrangement described above, Ti or the Ti alloy is used for the porous base of the anode 41. The metal material containing Ti is known as a material having low chemical reactivity and excellent corrosion resistance. However, if the alkaline electrolytic solution is used as the anode solution and an operation of the carbon dioxide electrolytic device 10 is continued for a long period of time, the porous base made of the metal material containing Ti is likely to be subjected to elution and the like caused by the alkaline electrolytic solution. The elution of Ti in the porous base causes clogging of pores of the porous base. This prevents passage of the gas and the electrolytic solution in the anode 41 and a reaction based thereon. The elution of Ti caused by the alkaline electrolytic solution becomes a main cause of deteriorating not only characteristics of the anode 41 but also characteristics of the electrolysis cell 20.

[0034] Accordingly, in the carbon dioxide electrolytic device 10 of the arrangement, in order to prevent the elution of Ti being a part of the composing material of the anode 41, caused by the alkaline electrolytic solution or the like, at least one selected from a configuration (1), a configuration (2), and a configuration (3) described below is adopted. At this time, any one of the configuration (1), the configuration (2), and the configuration (3) may be adopted, or two or more of the above configurations may be adopted in combination.

[0035] Configuration (1): An oxidant is added to the anode solution.

[0036] Configuration (2): An oxidant is added to the humidification water that humidifies the CO_2 gas.

[0037] Configuration (3): At least one selected from a group consisting of nitrogen dioxide (NO_2), nitrogen monoxide (NO), and ozone (O_3) is added to the CO_2 gas.

[0038] As the oxidant used in the configuration (1) and the configuration (2), there can be cited an oxidizing acid and hydrogen peroxide. As the oxidizing acid, there can be cited at least one selected from nitric acid, perchloric acid, chloric acid, chlorous acid, hypochlorous acid, chromic acid, dichromic acid, permanganic acid, arsenic acid, selenic acid, bromic acid, and iodic acid. These are capable of oxidizing a member that is in contact therewith, and thus can prevent the elution of Ti when the anode 41 containing Ti, for example, is brought into contact with the alkaline electrolytic solution. The same applies to hydrogen peroxide (H_2O_2), and it is possible to prevent, based on its oxidizing performance, the elution of Ti in the anode 41 containing Ti, caused by the alkaline electrolytic solution.

[0039] The prevention of Ti elution may be performed by not only the addition of the oxidant in a liquid state such as the oxidizing acid or hydrogen peroxide to the liquid such as the anode solution or the humidification water, but also the addition of gas such as NO_2, NO, or O_3 to the CO_2 gas, as described in the configuration (3). When NO_2 or NO is added to the CO_2 gas, it is converted into an oxidizing nitric acid (NHO_3). O_3 itself has an oxidizing performance. Also by using the CO_2 gas added with such an oxidizing gas or gas that is converted into the oxidizing gas, it is possible to prevent the elution of Ti in the anode 41 containing Ti, caused by the alkaline electrolytic solution, since the oxidizing gas or liquid permeates the anode 41 from the cathode 31 during the reaction of CO_2 gas.

[0040] In the configuration (1) and the configuration (2), a concentration of the oxidant added to the anode solution and the humidification water is preferably 0.1 mM or more and 100 mM (millimoles per liter) or less. If the concentration of the oxidant is less than 0.1 mM, there is a possibility that the effect of preventing the elution of Ti cannot be obtained sufficiently. Further, if the concentration of the oxidant exceeds 100 mM, there is a possibility that an adverse effect is exerted on the original characteristics of the anode solution and the humidification water. The concentration of the oxidant is more preferably 0.1 mM or more and 50 mM or less. Regarding the concentration of the oxidant in the electrolytic solution and the humidification water, it is possible to measure the types and the concentrations of various acids by an ion chromatography of solution, for example. The measurement can be performed in a similar manner in both a case where a measuring object is the electrolytic solution and a case where the measuring object is the humidification water.

[0041] When the configuration (3) is adopted, it is preferable that a gas concentration of at least one of NO_2, NO, and O_3 in the CO_2 gas is 10 ppb or more and 1000 ppm or less. If the above-described gas concentration is less than 10 ppb, there is a possibility that the effect of preventing the elution of Ti cannot be obtained sufficiently. Further, if the above-described gas concentration exceeds 1000 ppm, there is a possibility that an adverse effect is exerted on the characteristics of the CO_2 gas. The above-described gas concentration in the CO_2 gas is more preferably 100 ppb or more and 100 ppm or less. Regarding the contents of NO_2, NO, and NO_x in the gas, it is possible to perform trace measurement of NO and NO_2 by a high-sensitive NO_x analyzer for atmosphere (Model 42i-TL) manufactured by Thermo Fisher Scientific Inc., or the like, using a reduced-pressure chemiluminescence method, for example. It is possible to design such that an adjustment gas before being introduced into the cell is collected in a bag and the gas is introduced into a device to perform concentration measurement, or the gas is branched off from the middle of the pipe to be measured. Regarding the measurement of the concentration of ozone in the gas, it is possible to measure the ozone concentration in the gas by a high-precision ozone gas concentration meter using an ultraviolet absorption method, for example, ozone mate (OZG-3300/3500), or the like.

[0042] When adopting the above-described configuration (1), it is preferable to design such that the concentration of the oxidant in the anode solution is measured by the anode solution concentration measurement part 73 provided to the electrolytic solution supply unit 70, and the oxidant is added from the oxidant supply part 74 to the anode solution based on the measurement result, so that the concentration of the oxidant in the anode solution satisfies the above-described range. This makes it possible to maintain the concentration of the oxidant that decreases and increases when the anode solution is circulated. When adopting the configuration (2), the oxidant is added to the humidification water based on a measurement result obtained by a humidification water concentration measurement part that is provided according to need, so that the concentration of the oxidant in the humidification water satisfies the above-described range. The humidification water is required to be replenished since it decreases during an operation, and when performing the replenishment, the humidification water with adjusted oxidant concentration may be added, or the concentration may be measured in the anode solution concentration measurement part 73 to adjust an introduction amount of the oxidant. When adopting the configuration (3), it is possible to control the added amount of the oxidizing gas with respect to a flow rate of the CO_2 gas, by a flow rate of added oxidizing gas, so that the amount of oxidizing gas with respect to the CO_2 gas flow rate satisfies the above-described range.

[0043] As described above, when adopting the configuration (1), it is possible to adjust the concentration of the oxidant in the anode solution by using the anode solution concentration measurement part 73 and the oxidant supply part 74 provided to the electrolytic solution supply unit 70. When adopting the configuration (2), it is possible to adjust the concentration of the oxidant in the humidification water that is added to the CO_2 gas, by the humidification water concentration measurement part that is provided according to need. Alternatively, it is only required to previously adjust the concentration of the oxidant in the replenishing humidification water. At this time, the humidification water concentration measurement part may be provided or may not be provided. When adopting the configuration (3), it is possible to adjust the flow rate of added oxidizing gas, and thus a concentration measurement part of the oxidizing gas in the CO_2 gas may not be provided or may be provided according to need. When adopting the configuration (1) or the configuration (3), it is possible to consider a case where a configuration of adding no humidification water to the CO_2 gas is adopted depending on circumstances. In such a case, it is possible to adopt the gas supply unit 60 that does not include the humidification part 62 or the liquid pouring part (liquid pouring pipe) 65 as the humidification water supply part.

[0044] As described above, according to the carbon dioxide electrolytic device 10 of the arrangement, it is possible to prevent the elution of Ti when the anode 41 containing Ti is brought into contact with the alkaline electrolytic solution, by adding the oxidant to the anode solution, adding the oxidant to the humidification water that humidifies the CO_2 gas, or adding at least one selected from a group consisting of NO_2, NO, and O_3 to the CO_2 gas. Therefore, it becomes possible to prevent clogging of pores due to the elution of the porous base containing Ti of the anode 41, the deterioration of characteristics of the anode 41 caused thereby, and the deterioration of characteristics of the electrolysis cell 20 as well. The characteristics of the electrolysis cell 20 can be maintained over a long period of time.

EXAMPLES

[0045] Next, examples and evaluation results thereof will be described.

(Example 1)

[0046] First, as composing materials of a cathode catalyst layer, catalytic particles in which Au nanoparticles (metal catalyst) each having an average diameter of 2 nm were supported on carbon particles, and a Nafion solution (product name, manufactured by Du Pont) as an ion-conductive material (ion-exchange resin) were prepared. The materials, pure water, and isopropanol were mixed at a predetermined ratio, to thereby prepare a catalyst coating solution.

[0047] As an electrode base, a sheet of carbon paper with a diffusion layer having a microporous layer was prepared. A spray nozzle was filled with the above-described catalyst coating solution, and the solution was sprayed on the carbon paper disposed on a heated hot plate to perform spray coating. The spray coating of the catalyst coating solution was performed so that a thickness of a cathode became 55 μm. Further, a mass of the metal catalyst per unit area of the catalyst layer was set to 0.15 mg/cm^2. This coated carbon paper was cut into a size of 4 × 4 cm to obtain the cathode (an electrode area: 16 cm^2).

[0048] As an anode, an electrode in which a Ti nonwoven fabric was coated thereon with IrO_2 nanoparticles serving as a catalyst was used. This IrO_2/Ti nonwoven fabric was cut into 4 × 4 cm to obtain the anode. As a separator, a porous membrane of polyethersulfone was used.

[0049] Next, an electrolysis cell illustrated in FIG. 1 was fabricated. A cathode current collector, a CO_2 gas flow path, the cathode, the separator, the anode, an anode solution flow path, and an anode current collector were stacked in this order from the top, sandwiched by non-illustrated support plates, and further tightened by bolts, to thereby fabricate the electrolysis cell. The anode current collector and the cathode current collector were connected to an external power supply, an electrolytic solution added with nitric acid of 3 millimoles per liter (mM) (a pH of the electrolytic solution when starting measurement was 7.5 to 8.5) was made to flow through the anode solution flow path, and a CO_2 gas was made to flow through a cathode gas flow path, to thereby fabricate a carbon dioxide electrolytic device illustrated in FIG. 1.

(Example 2)

[0050] An electrolysis cell and an electrolytic device illustrated in FIG. 1 were fabricated in a manner similar to that in the example 1, except that a humidification water supply device disposed at a pre-stage of the cathode gas flow path of the electrolytic device in the example 1 was used to add nitric acid of 10 millimoles per liter (mM) to the humidification water, and no nitric acid was added to the electrolytic solution.

(Examples 3 to 9)

[0051] Electrolysis cells and electrolytic devices illustrated in FIG. 1 or FIG. 2 were fabricated in a manner similar to that in the example 1, except that conditions described in Table 1 (the destination to which the additive was added, the type of additive and the added amount, and the pH of the electrolytic solution when starting measurement) were respectively adopted.

[0052] Next, the electrolytic devices of the examples 1 to 9 were operated under the following conditions. CO_2 or gas obtained by adding the additive described in Table 1 to CO_2 was humidified by water or water added with the additive described in Table 1 and the humidified gas was supplied by a predetermined amount to the CO_2 gas flow path, and an electrolytic solution (an aqueous solution of sodium hydrogen carbonate with a concentration of 0.1 M) or a liquid obtained by adding the additive described in Table 1 to the electrolytic solution, was supplied to the anode solution flow path. A constant current of 200 mA/cm^2 was continuously applied between the anode and the cathode to perform the operation for 1000 hours. When the separator after the operation of 1000 hours was taken out and titanium was analyzed through the XRF (fluorescent X-ray analysis), titanium was not detected almost at all in the examples. A CO Faradaic efficiency after the operation of 1000 hours was also maintained to 80% or more.

(Comparative example 1)

[0053] An electrolysis cell and an electrolytic device illustrated in FIG. 1 were fabricated in a manner similar to that in the example 1, except that no nitric acid was added to the electrolytic solution in the example 1.

(Comparative examples 2 and 3)

[0054] Electrolysis cells and electrolytic devices were fabricated under conditions similar to those in the example 1, except that conditions described in Table 1 were adopted.

[0055] When an operation test of the electrolytic devices of the comparative examples 1 to 3 was performed under the same conditions as those of the example 1 and titanium in the separators was analyzed by the XRF in a similar manner, in the comparative examples 1 and 2, the titanium element was detected from a land portion, and thus it was confirmed that titanium was eluted from the anode and diffused in the separator. In the comparative example 3, a deterioration of the cell occurred due to the high concentration of acid in the electrolytic solution, and thus it was not possible to perform the long-time operation of 1000 hours.

Table 1

	Electrolytic solution		Humidification water		CO_2 gas		pH of electrolytic solution
	Additive	Added amount (mM)	Additive	Added amount (mM)	Additive	Added amount (ppm)	
Example 1	Nitric acid	3	None	-	None	-	7.5-8.5
Example 2	None	-	Nitric acid	10	None	-	7.5-8.5
Example 3	None	-	None	-	NOx	15	7.5-8.5
Example 4	Nitric acid	0.5	Nitric acid	5	None	-	7.5-8.5
Example 5	Nitric acid	10	None	-	NOx	10	7.5-8.5
Example 6	Hypochlorous acid	5	None	-	None	-	7.5-8.5
Example 7	Hydrogen peroxide solution	15	None	-	None	-	7.5-8.5
Example 8	Nitric acid	50	None	-	None	-	6.5-7.5
Example 9	Nitric acid	20	Nitric acid	5	NOx	10	6.5-7.5
Com parative example 1	None	-	None	-	None	-	7.5-8.5
Com parative example 2	Nitric acid	0.01	None	-	None	-	7.5-8.5
Com parative example 3	Nitric acid	1000	None	-	None	-	0-1.0

[0056] Note that configurations of the respective arrangements may be each adopted in combination, and further may be partially substituted. Herein, while certain arrangements of the present invention have been described, these arrangements have been presented by way of example only, and are not intended to limit the scope of the inventions. Indeed, the novel arrangements described herein may be embodied in a variety of other forms; furthermore, various omissions, substitutions, and changes in the form of the arrangements described herein may be made without departing from the spirit of the inventions. The accompanying claims and their equivalents are intended to cover such forms or modifications as would fall within the scope and spirit of the invention.

[0057] Clauses of the above-described arrangements will be described below.

[0058] Clause 1: A carbon dioxide electrolytic device, comprising:

an electrolysis cell including a cathode configured to reduce carbon dioxide to produce a carbon compound, an anode configured to oxidize water or hydroxide ion to produce oxygen and having a base containing titanium, a cathode flow path configured to supply carbon dioxide to the cathode, an anode flow path configured to supply an electrolytic solution containing water to the anode, and a separator configured to separate the anode and the cathode;

a gas supply unit configured to supply carbon dioxide to the cathode flow path;

at least either of a humidifier configured to humidify carbon dioxide supplied to the cathode flow path by using a humidification water, and a liquid pouring part configured to add the humidification water to the carbon dioxide; and an electrolytic solution supply unit configured to supply the electrolytic solution to the anode flow path, wherein at least either of the electrolytic solution and the humidification water contains an oxidant; and/or the carbon dioxide gas supplied to the cathode flow path contains at least one selected from a group consisting of nitrogen dioxide, nitrogen monoxide, and ozone.

[0059] Clause 2: The device according to clause 1, wherein
the oxidant is at least one selected from a group consisting of an oxidizing acid and hydrogen peroxide.

[0060] Clause 3: The device according to clause 2, wherein
the oxidizing acid includes at least one selected from a group consisting of nitric acid, perchloric acid, chloric acid, chlorous acid, hypochlorous acid, chromic acid, dichromic acid, permanganic acid, arsenic acid, selenic acid, bromic acid, and iodic acid.

[0061] Clause 4. The carbon dioxide electrolytic device according to any one of clause 1 to clause 3, wherein
a concentration of the oxidant in the electrolytic solution or the humidification water is 0.1 mM or more and 100 mM or less.

[0062] Clause 5: The device according to clause 1, wherein
a concentration of at least one selected from the group consisting of nitrogen dioxide, nitrogen monoxide, and ozone in the carbon dioxide gas is 10 ppb or more and 1000 ppm or less.

[0063] Clause 6: The device according to any one of clause 1 to clause 5, wherein
the electrolytic solution has a pH of 6 or more and 10 or less.

[0064] Clause 7: The device according to any one of clause 1 to clause 6, further comprising a measurement part configured to measure a concentration of the oxidant in the electrolytic solution or the humidification water.

[0065] Clause 8: The device according to any one of clause 1 to clause 7, wherein
the separator includes a porous membrane.

[0066] Clause 9: A carbon dioxide electrolytic device, comprising:

an electrolysis cell including a cathode configured to reduce carbon dioxide to produce a carbon compound, an anode configured to oxidize water or hydroxide ion to produce oxygen and having a base containing titanium, a cathode flow path configured to supply carbon dioxide to the cathode, an anode flow path configured to supply an electrolytic solution containing water to the anode, and a separator configured to separate the anode and the cathode;
a gas supply unit configured to supply carbon dioxide to the cathode flow path; and
an electrolytic solution supply unit configured to supply the electrolytic solution to the anode flow path, wherein the electrolytic solution a contains an oxidant.

[0067] Clause 10: A carbon dioxide electrolytic device, comprising:

an electrolysis cell including a cathode configured to reduce carbon dioxide to produce a carbon compound, an anode configured to oxidize water or hydroxide ion to produce oxygen and having a base containing titanium, a cathode flow path configured to supply carbon dioxide to the cathode, an anode flow path configured to supply an electrolytic solution containing water to the anode, and a separator configured to separate the anode and the cathode;
a gas supply unit configured to supply carbon dioxide to the cathode flow path;
at least either of a humidifier configured to humidify carbon dioxide supplied to the cathode flow path by using a humidification water, and a liquid pouring part configured to add the humidification water to the carbon dioxide; and
an electrolytic solution supply unit configured to supply the electrolytic solution to the anode flow path, wherein the humidification water contains an oxidant.

[0068] Clause 11: A carbon dioxide electrolytic device, comprising:

an electrolysis cell including a cathode configured to reduce carbon dioxide to produce a carbon compound, an anode configured to oxidize water or hydroxide ion to produce oxygen and having a base containing titanium, a cathode flow path configured to supply carbon dioxide to the cathode, an anode flow path configured to supply an electrolytic solution containing water to the anode, and a separator configured to separate the anode and the cathode;
a gas supply unit configured to supply carbon dioxide to the cathode flow path; and
an electrolytic solution supply unit configured to supply the electrolytic solution to the anode flow path, wherein the carbon dioxide gas supplied to the cathode flow path contains at least one selected from a group consisting of nitrogen dioxide, nitrogen monoxide, and ozone.

[0069] Clause 12: A method of electrolyzing carbon dioxide, comprising:

supplying humidified carbon dioxide to a cathode of an electrolysis cell via a cathode flow path, and supplying an

electrolytic solution to an anode having a base containing titanium of the electrolysis cell via an anode flow path; and
supplying a current to the cathode and the anode, and reducing carbon dioxide to produce a carbon compound, wherein
an oxidant is added to at least one of the electrolytic solution and a humidification water used for humidifying carbon dioxide; and/or at least one selected from a group consisting of nitrogen dioxide, nitrogen monoxide, and ozone is added to the carbon dioxide gas supplied to the cathode flow path.

[0070] Clause 13: The method according to clause 12, wherein
the oxidant is at least one selected from a group consisting of an oxidizing acid and hydrogen peroxide.

[0071] Clause 14: The method according to clause 13, wherein
the oxidizing acid includes at least one selected from a group consisting of nitric acid, perchloric acid, chloric acid, chlorous acid, hypochlorous acid, chromic acid, dichromic acid, permanganic acid, arsenic acid, selenic acid, bromic acid, and iodic acid.

[0072] Clause 15: The method according to any one of clause 12 to clause 14, wherein
to the electrolytic solution or the humidification water, the oxidant is added at a concentration of 0.1 mM or more and 100 mM or less.

[0073] Clause 16: The method according to clause 12, wherein
to the carbon dioxide gas, at least one selected from the group consisting of nitrogen dioxide, nitrogen monoxide, and ozone is added at a concentration of 10 ppb or more and 1000 ppm or less.

[0074] Clause 17: The method according to any one of clause 12 to clause 16, wherein
the electrolytic solution has a pH of 6 or more and 10 or less.

[0075] Clause 18: A method of electrolyzing carbon dioxide, comprising:

supplying carbon dioxide to a cathode of an electrolysis cell via a cathode flow path, and supplying an electrolytic solution to an anode having a base containing titanium of the electrolysis cell via an anode flow path; and
supplying a current to the cathode and the anode, and reducing carbon dioxide to produce a carbon compound, wherein
an oxidant is added to the electrolytic solution.

[0076] Clause 19: A method of electrolyzing carbon dioxide, comprising:

supplying humidified carbon dioxide to a cathode of an electrolysis cell via a cathode flow path, and supplying an electrolytic solution to an anode having a base containing titanium of the electrolysis cell via an anode flow path; and
supplying a current to the cathode and the anode, and reducing carbon dioxide to produce a carbon compound, wherein
an oxidant is added to a humidification water used for humidifying carbon dioxide.

[0077] Clause 20: A method of electrolyzing carbon dioxide, comprising:

supplying carbon dioxide to a cathode of an electrolysis cell via a cathode flow path, and supplying an electrolytic solution to an anode having a base containing titanium of the electrolysis cell via an anode flow path; and
supplying a current to the cathode and the anode, and reducing carbon dioxide to produce a carbon compound, wherein
at least one selected from a group consisting of nitrogen dioxide, nitrogen monoxide, and ozone is added to the carbon dioxide gas supplied to the cathode flow path.

Claims

1. A carbon dioxide electrolytic device, comprising:

an electrolysis cell including a cathode configured to reduce carbon dioxide to produce a carbon compound, an anode configured to oxidize water or hydroxide ion to produce oxygen and having a base containing titanium, a cathode flow path configured to supply carbon dioxide to the cathode, an anode flow path configured to supply an electrolytic solution containing water to the anode, and a separator configured to separate the anode and the cathode;
a gas supply unit configured to supply carbon dioxide to the cathode flow path;
at least one of a humidifier configured to humidify carbon dioxide supplied to the cathode flow path by using a

humidification water, and a liquid pouring part configured to add the humidification water to the carbon dioxide; and

an electrolytic solution supply unit configured to supply the electrolytic solution to the anode flow path, wherein

at least one of the electrolytic solution and the humidification water contains an oxidant; and/or

the carbon dioxide gas supplied to the cathode flow path contains at least one selected from a group consisting of nitrogen dioxide, nitrogen monoxide, and ozone.

2. The device according to claim 1, wherein
the oxidant is at least one selected from a group consisting of an oxidizing acid and hydrogen peroxide.

3. The device according to claim 2, wherein
the oxidizing acid includes at least one selected from a group consisting of nitric acid, perchloric acid, chloric acid, chlorous acid, hypochlorous acid, chromic acid, dichromic acid, permanganic acid, arsenic acid, selenic acid, bromic acid, and iodic acid.

4. The device according to any one of claim 1 to claim 3, wherein
a concentration of the oxidant in at least one of the electrolytic solution and the humidification water is 0.1 mM or more and 100 mM or less.

5. The device according to claim 1, wherein
a concentration of at least one selected from the group consisting of nitrogen dioxide, nitrogen monoxide, and ozone in the carbon dioxide gas is 10 ppb or more and 1000 ppm or less.

6. The device according to any one of claim 1 to claim 5, wherein
the electrolytic solution has a pH of 6 or more and 10 or less.

7. The device according to any one of claim 1 to claim 6, further comprising a measurement part configured to measure a concentration of the oxidant in at least one of the electrolytic solution and the humidification water.

8. The device according to any one of claim 1 to claim 7, wherein
the separator includes a porous membrane.

9. A method of electrolyzing carbon dioxide, comprising:

supplying humidified carbon dioxide to a cathode of an electrolysis cell via a cathode flow path, and supplying an electrolytic solution to an anode having a base containing titanium of the electrolysis cell via an anode flow path; and

supplying a current to the cathode and the anode, and reducing carbon dioxide to produce a carbon compound, wherein

an oxidant is added to at least one of the electrolytic solution and a humidification water used for humidifying carbon dioxide; and/or

at least one selected from a group consisting of nitrogen dioxide, nitrogen monoxide, and ozone is added to the carbon dioxide gas supplied to the cathode flow path.

10. The method according to claim 9, wherein
the oxidant is at least one selected from a group consisting of an oxidizing acid and hydrogen peroxide.

11. The method according to claim 10, wherein
the oxidizing acid includes at least one selected from a group consisting of nitric acid, perchloric acid, chloric acid, chlorous acid, hypochlorous acid, chromic acid, dichromic acid, permanganic acid, arsenic acid, selenic acid, bromic acid, and iodic acid.

12. The method according to any one of claim 9 to claim 11, wherein
to at least either of the electrolytic solution and the humidification water, the oxidant is added at a concentration of 0.1 mM or more and 100 mM or less.

13. The method according to claim 9, wherein
to the carbon dioxide gas, at least one selected from the group consisting of nitrogen dioxide, nitrogen monoxide, and ozone is added at a concentration of 10 ppb or more and 1000 ppm or less.

14. The method according to any one of claim 9 to claim 13, wherein
the electrolytic solution has a pH of 6 or more and 10 or less.

FIG. 1

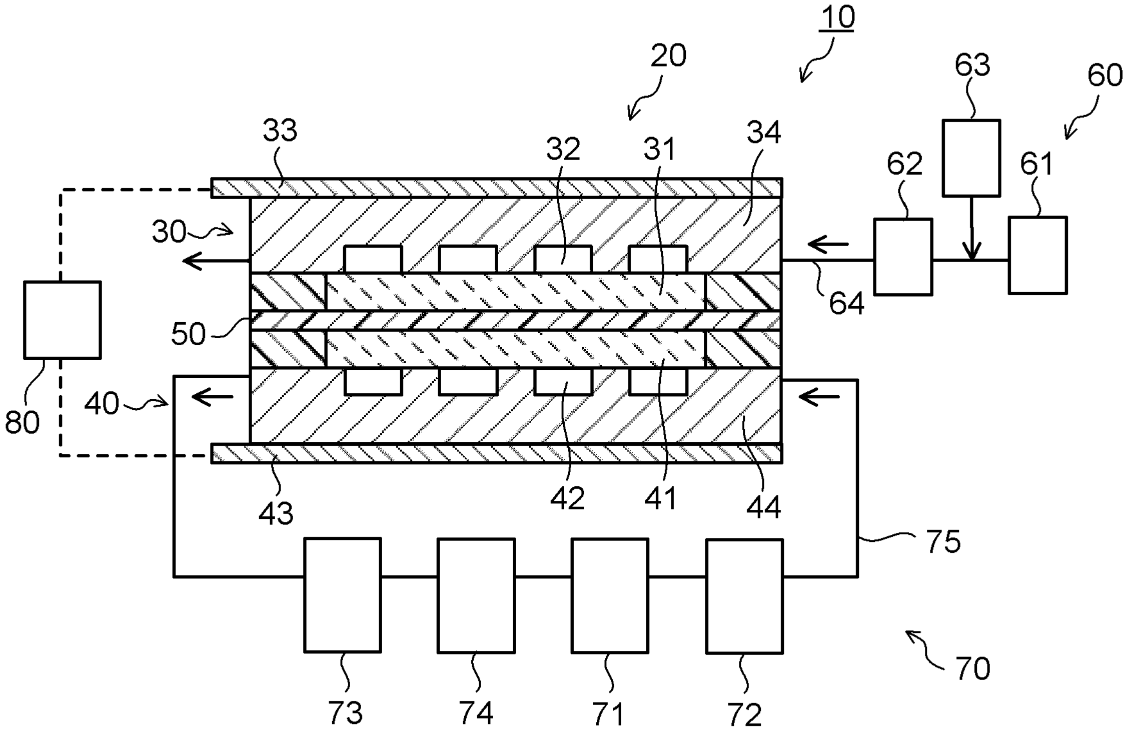
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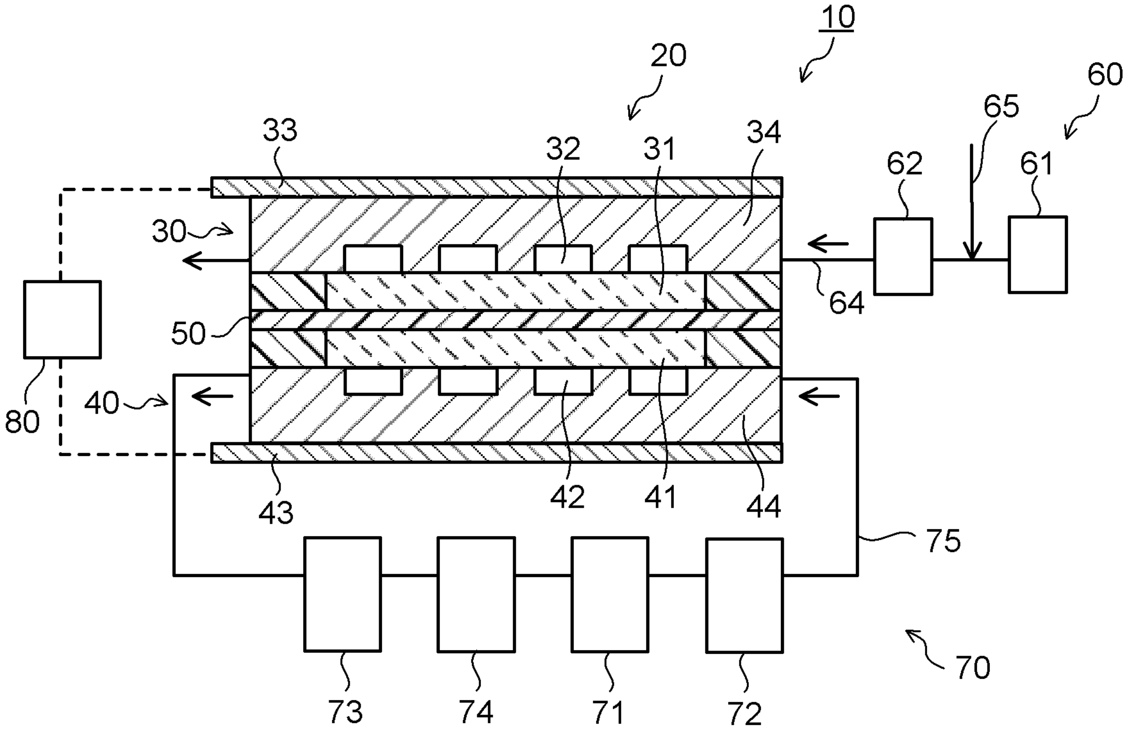
FIG. 2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