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(54) **ELECTROCHEMICAL REACTION DEVICE AND METHOD OF OPERATING
ELECTROCHEMICAL REACTION DEVICE**

(57) An electrochemical reaction device includes: a structure that includes: a cathode; an anode; a diaphragm, a cathode chamber; and an anode chamber; a first to a fourth flow path through which a first to fourth fluid flows respectively; at least one controller selected from a first and a second flow rate controller, a first and a second pressure controller, a temperature controller and a power supply, the controller including the first flow rate

controller; a gas/liquid separator in the middle of the fourth flow path; a first flowmeter that measures a flow rate of the third fluid; a second flowmeter that measures a flow rate of the fourth fluid; and a control device that measures the sum of the flow rates of the first, third and fourth fluids and controls the controller according to the sum to control a pressure difference between the chambers.

Description

FIELD

5 **[0001]** Arrangements relate to an electrochemical reaction device.

BACKGROUND

10 **[0002]** In recent years, fossil fuels such as petroleum and coal may be depleted, and alternately sustainable renewable energy has been increasingly expected. Such energy problems and environmental problems motivate to develop a Power to Chemicals (P2C) technology to electrochemically reduce carbon dioxide using the renewable energy such as sunlight or the like to generate a storable chemical energy source. Electrolytic devices with the P2C technology are included in the electrochemical reaction devices such as carbon dioxide reaction devices, the carbon dioxide reaction devices include for example, an anode to oxidize water (H_2O) to produce oxygen (O_2) and a cathode to reduce carbon dioxide (CO_2) to produce a carbon compound. The anode and the cathode of the carbon dioxide reaction device are connected to a power supply using renewable energy such as solar power generation, hydroelectric power generation, wind power generation, geothermal power generation, or the like.

15 **[0003]** The cathode of the carbon dioxide reaction device is arranged, for example, to be immersed in water containing dissolved carbon dioxide or to be in contact with carbon dioxide flowing through a flow path. The cathode obtains reduction potential for carbon dioxide from the power supply derived from renewable energy and thereby reduces carbon dioxide to produce carbon compounds such as carbon monoxide (CO), formic acid (HCOOH), methanol (CH_3OH), methane (CH_4), ethanol (C_2H_5OH), ethane (C_2H_6), ethylene (C_2H_4), formaldehyde (HCHO), ethylene glycol ($C_2H_6O_2$), acetic acid (CH_3COOH), and propanol (C_3H_7OH). The anode is arranged to be in contact with an electrolytic solution containing water and produces oxygen and a hydrogen ion (H^+). Such a carbon dioxide reaction device is required to increase the use efficiency of carbon dioxide, as well as the use efficiency and the utility value of reduction products of carbon dioxide.

RELEVANT REFERENCES

Patent Reference

30 **[0004]**

Reference 1: JP 2019-506165 A

Reference 2: JP 2018-070936 A

35 Reference 3: JP 2021-46574 A

BRIEF DESCRIPTION OF THE DRAWINGS

[0005]

40 FIG. 1 is a schematic view illustrating an example configuration of an electrochemical reaction device in an arrangement;
 FIG. 2 is a schematic view illustrating another example configuration of the electrochemical reaction device in the arrangement;
 45 FIG. 3 is a schematic view illustrating another example configuration of the electrochemical reaction device in the arrangement;
 FIG. 4 is a schematic view illustrating another example configuration of the electrochemical reaction device in the arrangement;
 FIG. 5 is a schematic view illustrating another example configuration of the electrochemical reaction device in the arrangement; and
 50 FIG. 6 is a schematic view illustrating another example configuration of the electrochemical reaction device in the arrangement.

DETAILED DESCRIPTION

55 **[0006]** An electrochemical reaction device in an arrangement includes: an electrochemical reaction structure that includes: a cathode having a reduction catalyst that promotes a reduction reaction of reducing carbon dioxide to produce a carbon compound; an anode having an oxidation catalyst that promotes an oxidation reaction of oxidizing water to produce

oxygen; a diaphragm between the cathode and the anode, a cathode chamber facing on the cathode; and an anode chamber facing on the anode; a first flow path through which a first fluid flows, the first flow path being connected to an inlet of the cathode chamber, and the first fluid being supplied to the cathode chamber and containing the carbon dioxide; a second flow path through which a second fluid flows, the second flow path being connected to an inlet of the anode chamber, the second fluid being supplied to the anode chamber and containing the water; a third flow path through which a third fluid flows, the third flow path being connected to an outlet of the cathode chamber, and the third fluid being discharged from the cathode chamber and containing the carbon compound; a fourth flow path through which a fourth fluid flows, the fourth flow path being connected to an outlet of the anode chamber, and the fourth fluid being discharged from the anode chamber and containing the water and the oxygen; at least one controller selected from the group consisting of a first flow rate controller, a second flow rate controller, a first pressure controller, a second pressure controller, a temperature controller and a power supply, the first flow rate controller being configured to control a flow rate of the first fluid flowing through the first flow path, the second flow rate controller being configured to control a flow rate of the second fluid flowing through the second flow path, the first pressure controller being configured to control a pressure of the third flow path, the second pressure controller being configured to control a pressure of the fourth flow path, the temperature controller being configured to control a temperature of the electrochemical reaction structure, and the power supply being configured to control a current or a voltage to be supplied to the electrochemical reaction structure, the at least one controller including the first flow rate controller; a gas/liquid separator provided in the middle of the fourth flow path and configured to process the fourth fluid to separate a liquid containing the water from the fourth fluid; a first flowmeter configured to measure a flow rate of the third fluid flowing through the third flow path; a second flowmeter configured to measure a flow rate of the processed fourth fluid flowing through the fourth flow path; and a control device connected to the at least one controller, the first flowmeter and the second flowmeter, the control device being configured to measure a sum of the flow rate of the first fluid flowing through the first flow path, the flow rate of the third fluid flowing through the third flow path, and the flow rate of the processed fourth fluid flowing through the fourth flow path, and being configured to control the at least one controller according to the sum to control a pressure difference between the cathode chamber and the anode chamber.

[0007] There will be explained arrangements with reference to the drawings below. In each of the following arrangements, substantially the same components are denoted by the same reference numerals and symbols, and explanations thereof may be partly omitted. The drawings are schematic, and a relation between thickness and planar dimension, a thickness ratio among parts, and so on may be different from actual ones.

[0008] In this specification, "connecting" includes not only directly connecting but also indirectly connecting in some cases, unless otherwise specified.

[0009] FIG. 1 is a schematic view illustrating an example configuration of an electrochemical reaction device. FIG. 1 illustrates an example configuration of an electrochemical reaction device 1. The electrochemical reaction device 1 includes an electrochemical reaction structure 10, a flow path P1, a flow path P2, a flow path P3, a flow path P4, a flow rate controller 21, a flow rate controller 22, a humidifier 30, a pressure controller 41, a pressure controller 42, a dehydrator 51, a gas/liquid separator 52, a flowmeter 61, a flowmeter 62, a power supply 70, and a control device 80.

[0010] The electrochemical reaction structure 10 includes a cathode 11, an anode 12, a diaphragm 13, a flow path plate 14, a flow path plate 15, a current collector 16, and a current collector 17.

[0011] The cathode 11 is, for example, a reduction electrode for performing a reduction reaction of at least one reducible material (substance to be reduced). Examples of the at least one reducible material include carbon dioxide. The cathode 11 can reduce, for example, carbon dioxide supplied as a gas or carbon dioxide contained in a first electrolytic solution (cathode solution) to produce a carbon compound. Examples of the carbon compound include carbon monoxide, formic acid, methanol, methane, ethanol, ethane, ethylene, formaldehyde, ethylene glycol, acetic acid, and propanol. The cathode 11 may perform a side reaction of generating hydrogen through a reduction reaction of water as well as a reduction reaction of carbon dioxide.

[0012] The cathode 11 has a reduction catalyst that promotes a reduction reaction that reduces carbon dioxide to produce a carbon compound, for example. The reduction catalyst can be formed using a material that reduces the activation energy for reducing carbon dioxide, for example. In other words, the reduction catalyst can be formed using a material that lowers the overvoltage when producing a carbon compound by the reduction reaction of carbon dioxide, for example.

[0013] The cathode 11 can be formed using a metal material or a carbon material, for example. Examples of the metal material include metals such as gold, aluminum, copper, silver, platinum, palladium, zinc, mercury, indium, nickel, and titanium, alloys containing these metals, and so on. Examples of the carbon material include graphene, carbon nanotube (CNT), fullerene, ketjen black, and so on. The cathode 11 is not limited to these materials, and may be formed using a metal complex such as a Ru complex or a Re complex, or an organic molecule having an imidazole skeleton or a pyridine skeleton, for example. The cathode 11 may be formed using a mixture of a plurality of materials. The cathode 11 may have a structure having the reduction catalyst in a thin film shape, a mesh shape, a particle shape, a wire shape, or the like provided on a conductive substrate, for example. The type of the carbon compound produced by the reduction reaction also differs depending on the type of reduction catalyst.

[0014] The anode 12 is an oxidation electrode for performing an oxidation reaction of at least one oxidizable material (substance to be oxidized), for example. Examples of at least one oxidizable material include water. The anode 12 oxidizes an oxidizable material such as a substance or ion in a second electrolytic solution (anode solution) to produce oxygen, for example.

[0015] The anode 12 has an oxidation catalyst that promotes an oxidation reaction that oxidizes water to produce oxygen, for example. The oxidation catalyst can be formed using a material that reduces the activation energy when oxidizing an oxidizable material, in other words, a material that lowers the reaction overpotential, for example. Examples of the oxidation reaction at the anode 12 include reactions of oxidizing water to produce oxygen or hydrogen peroxide water, oxidizing chloride ions (Cl^-) to produce chlorine, oxidizing carbonate ions or hydrogen carbonate ions to produce carbon dioxide, and so on.

[0016] Examples of the oxidation catalyst include metal materials. Examples of the metal material include ruthenium, iridium, platinum, cobalt, nickel, iron, manganese, tantalum, zirconium, and so on. Further, examples of the metal material include a binary metal oxide, a ternary metal oxide, a quaternary metal oxide, and so on. Examples of the binary metal oxide include 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), and so on. Examples of the ternary metal oxide include nickel-iron oxide (Ni-Fe-O), nickel-cobalt oxide (Ni-Co-O), lanthanum-cobalt oxide (La-Co-O), nickel-lanthanum oxide (Ni-La-O), strontium-iron oxide (Sr-Fe-O), and so on. Examples of the quaternary metal oxide include lead-ruthenium-iridium oxide (Pb-Ru-Ir-O), lanthanum-strontium-cobalt oxide (La-Sr-Co-O), and so on. The oxidation catalyst is not limited to these materials, and may be formed using a metal hydroxide containing a metal such as cobalt, nickel, iron, or manganese, or a metal complex such as a ruthenium complex or an iron complex. Further, the oxidation catalyst may be formed by mixing a plurality of materials.

[0017] The anode 12 may be formed using a composite material containing both an oxidation catalyst and a conductive material. Examples of the conductive material include carbon materials such as carbon black, activated carbon, fullerene, carbon nanotube, graphene, ketjen black, and diamond, transparent conductive oxides such as indium tin oxide (ITO), zinc oxide (ZnO), fluorine-doped tin oxide (FTO), aluminum-doped zinc oxide (AZO), and antimony-doped tin oxide (ATO), metals such as copper, aluminum, titanium, nickel, silver, tungsten, cobalt, and gold, alloys each containing at least one of the metals, and so on. The anode 12 may have a structure having the oxidation catalyst in a thin film shape, a mesh shape, a particle shape, a wire shape, or the like provided on a conductive substrate, for example. The conductive substrate can be formed using a metal material containing titanium, titanium alloy, or stainless steel, for example.

[0018] The diaphragm 13 is provided between the cathode 11 and the anode 12. The diaphragm 13 can separate a cathode chamber 140 and an anode chamber 150. The diaphragm 13 can move ions such as hydrogen ions (H^+), hydroxide ions (OH^-), hydrogen carbonate ions (HCO_3^-), and carbonate ions (CO_3^{2-}). By the diaphragm 13, an electrochemical reaction cell having a two-chamber structure can be formed. The diaphragm 13 may be provided in contact with the cathode 11 and the anode 12.

[0019] The diaphragm 13 can be formed using a membrane capable of selectively allowing anions or cations to pass therethrough, for example. This allows the composition of the second electrolytic solution in contact with the anode 12 to be different from that of the first electrolytic solution in contact with the cathode 11, and furthermore, differences in ionic strength, pH, and so on can promote the reduction reaction or the oxidation reaction. The diaphragm 13 may have a function of permeating part of ions contained in the electrolytic solutions in which the cathode 11 and the anode 12 are immersed therethrough, namely, a function of blocking one or more kinds of ions contained in the electrolytic solutions. This can differ the pH or the like between the two electrolytic solutions, for example. Further, in terms of the blocking of ions, a diaphragm that does not completely block part of ions but is effective enough to limit the amount of movement by ion species may be used.

[0020] The diaphragm 13 can be formed using an ion exchange membrane such as, for example, NEOSEPTA (registered trademark) of ASTOM Corporation, Selemon (registered trademark), Aciplex (registered trademark) of ASAHI GLASS CO., LTD., Fumasep (registered trademark), fumapem (registered trademark) of Fumatech GmbH, Nafion (registered trademark) being fluorocarbon resin made by sulfonating and polymerizing tetrafluoroethylene of E.I. du Pont de Nemours and Company, lewabrane (registered trademark) of LANXESS AG, IONSEP (registered trademark) of IONTECH Inc., Mustang (registered trademark) of PALL Corporation, ralex (registered trademark) of mega Corporation, Gore-Tex (registered trademark) of Gore-Tex Co., Ltd. Sustainion (registered trademark) of DIOXIDE MATERIALS, or PiperION (registered trademark) of Versogen, Inc. The ion exchange membrane may be formed using a membrane having hydrocarbon as a basic skeleton, for example. An anion exchange membrane may be formed using a membrane having an amine group, for example. In the case where there is a pH difference between the first electrolytic solution and the second electrolytic solution, by forming the diaphragm 13 using a bipolar membrane made by stacking a cation exchange membrane and an anion exchange membrane, the electrolytic solutions can be used while stably keeping the pHs thereof.

[0021] The diaphragm 13 may be formed using materials such as porous membranes of a silicone resin, fluorine-based resins such as perfluoroalkoxyalkane (PFA), perfluoroethylene propene copolymer (FEP), polytetrafluoroethylene (PTFE), ethylene-tetrafluoroethylene copolymer (ETFE), polyvinylidene fluoride (PVDF), polychlorotrifluoroethylene

(PCTFE), ethylene-chlorotrifluoroethylene copolymer (ECTFE), and polyethersulfone (PES), and ceramics, packing filled with glass filter, agar, and so on, insulating porous bodies of zeolite, oxide, and so on, for example. In particular, a hydrophilic porous membrane is preferable as the material for the diaphragm 13 because it can inhibit clogging due to air bubbles.

[0022] The cathode 11, the anode 12, and the diaphragm 13 are stacked to form an electrochemical reaction cell. The electrochemical reaction structure 10 may include a cell stack formed by stacking a plurality of electrochemical reaction cells. The presence of the cell stack increases the amount of carbon dioxide reacted per unit area to increase the production amount of carbon compounds. The number of stacked electrochemical reaction cells is preferably 10 or more and 150 or less, for example.

[0023] The flow path plate 14 defines the cathode chamber 140. The cathode chamber 140 is provided on the surface of the flow path plate 14 to face on the cathode 11 and can define a cathode flow path. The cathode chamber 140 has an inlet for supplying fluid to the cathode chamber 140 and an outlet for discharging the fluid from the cathode chamber 140. The surface shape of the cathode flow path is not limited in particular, but is serpentine, for example.

[0024] The flow path plate 15 defines the anode chamber 150. The anode chamber 150 is provided on the surface of the flow path plate 15 to face on the anode 12, and can define an anode flow path. The anode chamber 150 has an inlet for supplying fluid to the anode chamber 150 and an outlet for discharging the fluid from the anode chamber 150. The surface shape of the anode flow path is not limited in particular, but is serpentine, for example.

[0025] Electrolytic reactions such as an oxidation reaction and a reduction reaction by the electrochemical reaction structure 10 are preferably performed at a temperature of room temperature (for example, 25°C) or more and 100°C or less, at which the electrolytic solution does not vaporize. The temperature is preferably 60°C or more and 95°C or less, and more preferably 60°C or more and 80°C or less. In order to set the temperature to less than room temperature, a cooling device such as a chiller is required, which may reduce the energy efficiency of an overall system. When the temperature exceeds 100°C, the water in the electrolytic solution turns into vapor and resistance increases, which may reduce the electrolysis efficiency.

[0026] The current density of the cathode 11 is not limited in particular, but a higher current density is preferred in order to increase the amount of reduction products produced per unit area. The current density is preferably 100 mA/cm² or more and 1.5 A/cm² or less, and further preferably 300 mA/cm² or more 700 mA/cm² or less. When the current density is less than 100 mA/cm², the amount of reduction products produced per unit area is small, which requires a large area. When the current density exceeds 1.5 A/cm², a side reaction of hydrogen generation increases, leading to a decrease in the concentration of reduction products.

[0027] In the case where Joule heat also increases by increasing the current density, the temperature increases above an appropriate temperature, so that a cooling mechanism may be provided in or near the electrochemical reaction structure 10. The cooling mechanism may be water cooling or air cooling. Even when the temperature of the electrochemical reaction structure 10 is higher than room temperature, the temperature may remain unchanged as long as it is equal to or less than 100°C.

[0028] The flow path P1 is connected to the inlet of the cathode chamber 140. A cathode supply fluid to be supplied to the cathode chamber 140 can flow through the flow path P1. The cathode supply fluid contains carbon dioxide. The cathode supply fluid may be a gas containing gaseous carbon dioxide or the first electrolytic solution containing carbon dioxide.

[0029] The flow path P1 may be connected to a carbon dioxide supply source. The carbon dioxide supply source may include a carbon dioxide separation and capture device, and may be connected to the carbon dioxide separation and capture device. A carbon dioxide gas from the carbon dioxide separation and capture device can be supplied to the flow path P1, for example, directly or after being stored once. Examples of the carbon dioxide supply source include facilities having various incinerators or combustion furnaces such as a thermal power plant and a garbage incinerator, facilities having a steel plant and a blast furnace, and so on. The carbon dioxide supply source is not limited to these facilities, but may be other factories that generate carbon dioxide.

[0030] The flow path P2 is connected to the inlet of the anode chamber 150. An anode supply fluid to be supplied to the anode chamber 150 can flow through the flow path P2. The anode supply fluid contains water or the second electrolytic solution. The flow path P2 may be connected to an anode solution supply source. The anode solution supply source can supply the second electrolytic solution, which is used for the anode supply fluid, for example.

[0031] The flow path P3 is connected to the outlet of the cathode chamber 140. A cathode exhaust fluid to be discharged from the cathode chamber 140 can flow through the flow path P3. The cathode exhaust fluid contains a carbon compound and hydrogen produced by the reduction reaction at the cathode 11 and a part of the carbon dioxide gas or a part of the first electrolytic solution contained in the cathode supply fluid.

[0032] The flow path P4 is connected to the outlet of the anode chamber 150. An anode exhaust fluid to be discharged from the anode chamber 150 can flow through the flow path P4. The anode exhaust fluid contains, for example, gaseous oxygen produced by the oxidation reaction at the anode 12, carbon dioxide moving from the cathode chamber 140 or the electrolytic solution, and water or a part of the second electrolytic solution contained in the anode supply fluid.

[0033] When a gas containing a reducible material such as carbon dioxide (cathode gas) is supplied to the cathode

chamber 140, the electrochemical reaction structure 10 may include a second cathode chamber between the cathode 11 and the diaphragm 13 and supply the first electrolytic solution to the second cathode chamber. FIG. 2 is a schematic view illustrating another example configuration of the electrochemical reaction device in the arrangement. As illustrated in FIG. 2, the electrochemical reaction device 1 may further include a flow path plate 18, a cathode chamber 180, a flow path P5, and a flow path P6.

[0034] The flow path plate 18 defines the cathode chamber 180. The cathode chamber 180 is provided on the surface of the flow path plate 18 to face on the cathode 11, and can define a second cathode flow path. The cathode chamber 180 is arranged across the cathode 11 from the cathode chamber 140. The cathode chamber 180 has an inlet for supplying fluid to the cathode chamber 180 and an outlet for discharging the fluid from the cathode chamber 180.

[0035] The flow path P5 is connected to the inlet of the cathode chamber 180. A second cathode supply fluid to be supplied to the cathode chamber 180 can flow through the flow path P5. The second cathode supply fluid contains the first electrolytic solution. The first electrolytic solution may contain carbon dioxide, or does not need to contain carbon dioxide. The flow path P5 may be connected to a cathode solution supply source. The cathode solution supply source can supply the first electrolytic solution, which is used for the second cathode supply fluid, for example. When the first electrolytic solution is the same as the second electrolytic solution, the flow path P5 may be connected to the anode solution supply source.

[0036] The flow path P6 is connected to the outlet of the cathode chamber 180. A second cathode exhaust fluid to be discharged from the cathode chamber 180 can flow through the flow path P6. The second cathode exhaust fluid contains a carbon compound and hydrogen produced by the reduction reaction at the cathode 11 and the first electrolytic solution. The second cathode exhaust fluid may be reused by the gas/liquid separator separating the second cathode exhaust fluid into a gas component and a liquid component and then supplying the separated liquid component to the flow path P5 as the first electrolytic solution. In this case, the electrochemical reaction device 1 may include a flow path and a pump to return the separated liquid component to the flow path P5, the flow path connecting the flow path P5 and the flow path P6, the pump being provided in the middle of the flow path.

[0037] The first electrolytic solution preferably has a high absorptance of carbon dioxide. The carbon dioxide in the first electrolytic solution is not always limited to be dissolved therein, but be in an air bubble state to be mixed in the first electrolytic solution. Examples of the electrolytic solution containing carbon dioxide include aqueous solutions containing hydrogencarbonates and carbonates such as lithium hydrogen carbonate (LiHCO_3), sodium hydrogen carbonate (NaHCO_3), potassium hydrogen carbonate (KHCO_3), cesium hydrogen carbonate (CsHCO_3), sodium carbonate (Na_2CO_3), and potassium carbonate (K_2CO_3), phosphoric acid, boric acid, and so on. The electrolytic solution containing carbon dioxide may contain alcohols such as methanol or ethanol, or ketones such as acetone, or may be an alcohol solution or ketone solution. The first electrolytic solution may be an electrolytic solution containing a carbon dioxide absorbent that lowers the reduction potential for carbon dioxide, has a high ion conductivity, and absorbs carbon dioxide.

[0038] Examples of the electrolytic solutions such as the first electrolytic solution and the second electrolytic solution, include a solution containing water, which is, for example, an aqueous solution containing any electrolyte. The solution is preferred to be an aqueous solution that promotes the oxidation reaction of water. Examples of the aqueous solution containing the electrolyte include aqueous solutions containing phosphate ion (PO_4^{2-}), borate ion (BO_3^{3-}), sodium ion (Na^+), potassium ion (K^+), calcium ion (Ca^{2+}), lithium ion (Li^+), cesium ion (Cs^+), magnesium ion (Mg^{2+}), chloride ion (Cl^-), hydrogen carbonate ion (HCO_3^-), carbonate ion (CO_3^{2-}), hydroxide ion (OH^-), and so on.

[0039] Examples of the electrolytic solutions include an ionic liquid that is made of salts of cations such as imidazolium ions or pyridinium ions and anions such as BF_4^- or PF_6^- and is in a liquid state in a wide temperature range, or an aqueous solution thereof. Further, examples of other electrolytic solutions include amine solutions such as ethanolamine, imidazole, and pyridine, and aqueous solutions thereof. Examples of amine include primary amine, secondary amine, tertiary amine, and so on. The electrolytic solutions may be high in ion conductivity and have properties of absorbing carbon dioxide and characteristics of reducing the reduction energy.

[0040] Examples of the primary amine include methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, and so on. Hydrocarbons of the amine may be substituted by alcohol, halogen, and the like. Examples of amine whose hydrocarbons are substituted include methanolamine, ethanolamine, chloromethylamine, and so on. Further, an unsaturated bond may exist. These hydrocarbons are also the same in the secondary amine and the tertiary amine.

[0041] Examples of the secondary amine include dimethylamine, diethylamine, dipropylamine, dibutylamine, dipentylamine, dihexylamine, dimethanolamine, diethanolamine, dipropanolamine, and so on. The substituted hydrocarbons may be different. This also applies to the tertiary amine. Examples with different hydrocarbons include methylethylamine, methylpropylamine, and so on.

[0042] Examples of the tertiary amine include trimethylamine, triethylamine, tripropylamine, tributylamine, trihexylamine, trimethanolamine, triethanolamine, tripropanolamine, tributanolamine, trihexanolamine, methyldiethylamine, methyldipropylamine, and so on.

[0043] Examples of the cation of the ionic liquid include 1-ethyl-3-methylimidazolium ion, 1-methyl-3-propylimidazolium

ion, 1-butyl-3-methylimidazole ion, 1-methyl-3-pentylimidazolium ion, 1-hexyl-3-methylimidazolium ion, and so on.

[0044] A second place of the imidazolium ion may be substituted. Examples of the cation of the imidazolium ion whose second place is substituted include 1-ethyl-2,3-dimethylimidazolium ion, 1,2-dimethyl-3-propylimidazolium ion, 1-butyl-2,3-dimethylimidazolium ion, 1,2-dimethyl-3-pentylimidazolium ion, 1-hexyl-2,3-dimethylimidazolium ion, and so on.

[0045] Examples of the pyridinium ion include methylpyridinium, ethylpyridinium, propylpyridinium, butylpyridinium, pentylpyridinium, hexylpyridinium, and so on. In both of the imidazolium ion and the pyridinium ion, an alkyl group may be substituted, or an unsaturated bond may exist.

[0046] Examples of the anion include fluoride ion (F^-), chloride ion (Cl^-), bromide ion (Br^-), iodide ion (I^-), BF_4^- , PF_6^- , CF_3COO^- , $CF_3SO_3^-$, NO_3^- , SCN^- , $(CF_3SO_2)_3C^-$, bis(trifluoromethoxysulfonyl)imide, bis(perfluoroethylsulfonyl)imide, and so on. Dipolar ions in which the cations and the anions of the ionic liquid are coupled by hydrocarbons may be used. A buffer solution such as a potassium phosphate solution may be supplied to the anode chamber 150 and the cathode chamber 180.

[0047] The second electrolytic solution contains water as the oxidizable material. It is possible to change the amount of water or the electrolytic solution components contained in the first and second electrolytic solutions to change the reactivity and then change the selectivity of a reduced substance or the ratio of produced substances. The first and second electrolytic solutions may contain redox couples as needed. Examples of the redox couple include Fe^{3+}/Fe^{2+} , IO_3^-/I^- , and so on.

[0048] The flow rate controller 21 is provided in the middle of the flow path P1. The flow rate controller 21 can control the flow rate of the cathode supply fluid flowing through the flow path P1, for example. The flow rate controller 21 may include a mass flow controller, for example. The flow rate controller 21 can control the flow rate of carbon dioxide to be introduced into the cathode chamber 140. The flow rate controller 21 may have a function of controlling the flow rate of the cathode supply fluid based on a control signal from the control device 80. The flow rate controller 21 may, for example, measure the flow rate of the cathode supply fluid flowing through the flow path P1 and supply a data signal including data indicating the measured flow rate to the control device 80.

[0049] The flow rate controller 22 is provided in the middle of the flow path P2. The flow rate controller 22 can control the flow rate of the anode supply fluid flowing through the flow path P2, for example. The flow rate controller 22 may include a mass flow controller, for example. The flow rate controller 22 can also control the temperature of the electrochemical reaction structure 10 or move the gas generated in the anode chamber 150 to the flow path P4. The flow rate controller 22 may, for example, measure the flow rate of the anode supply fluid flowing through flow path P2 and supply a data signal including data indicating the measured flow rate to the control device 80.

[0050] The humidifier 30 is provided so as to precede or follow the flow rate controller 21 in the middle of the flow path P1. The humidifier 30 can humidify the carbon dioxide gas in the cathode supply fluid. Examples of the humidifier 30 include humidifiers such as a bubbling type humidifier and a hollow fiber membrane type humidifier. As illustrated in FIG. 1, arranging the humidifier 30 between the flow rate controller 21 and the cathode chamber 140 makes it possible to supply the cathode supply fluid containing a carbon dioxide gas to the cathode chamber 140 with an accurate supply amount even after humidification. The electrochemical reaction device in the arrangement does not need to include the humidifier 30.

[0051] The cathode supply fluid containing the humidified carbon dioxide gas may contain liquid in the form of mist or fumes. Apart of the cathode supply fluid containing the humidified carbon dioxide gas may consist of liquid water. Further, the water may contain something that functions as a cathode solution, or may contain carbon dioxide as the reducible substance.

[0052] The pressure controller 41 is provided in the middle of the flow path P3. The pressure controller 41 can control the pressure in the cathode chamber 140 by controlling the pressure of the flow path P3. The pressure controller 41 may have a function of controlling the pressure in the cathode chamber 140 based on a control signal from the control device 80. The pressure controller 41 may have a function of indirectly measuring the pressure in the cathode chamber 140 by measuring the pressure of the flow path P3.

[0053] The pressure controller 42 is provided in the middle of the flow path P4. The pressure controller 42 can control the pressure in the anode chamber 150 by controlling the pressure of the flow path P4, for example. The pressure controller 42 may have a function of controlling the pressure in the anode chamber 150 based on a control signal from the control device 80. The pressure controller 42 may have a function of indirectly measuring the pressure in the anode chamber 150 by measuring the pressure of the flow path P4.

[0054] The dehydrator 51 is provided so as to follow the pressure controller 41, for example, in the middle of the flow path P3. The dehydrator 51 can, for example, process the cathode exhaust fluid to separate water and the first electrolytic solution from the cathode exhaust fluid. The dehydrator 51 may have a function of removing water from exhaust gas by cooling or the like. The arrangement of the dehydrator 51 preceding the flowmeter 61 makes it possible to more accurately measure the flow rate of gas containing carbon compounds in the cathode exhaust fluid discharged from the cathode chamber 140.

[0055] The gas/liquid separator 52 is provided so as to follow the pressure controller 42, for example, in the middle of the flow path P4. The gas/liquid separator 52 can, for example, process the anode exhaust fluid to separate liquid such as

water and the electrolytic solution from the anode exhaust fluid. The processed anode exhaust fluid contains, for example, oxygen produced by the oxidation reaction at the anode 12 and carbon dioxide that has moved from the cathode chamber 140. The arrangement of the gas/liquid separator 52 preceding the flowmeter 62 makes it possible to more accurately measure the flow rate of gas such as oxygen or carbon dioxide in the anode exhaust fluid discharged from the anode chamber 150.

[0056] The flowmeter 61 is provided so as to follow the dehydrator 51, for example, in the middle of the flow path P3. The flowmeter 61 can measure the flow rate of the processed cathode exhaust fluid flowing through the flow path P3, for example. The flowmeter 61 can measure the total flow rate of gases such as carbon compounds, hydrogen, and unreacted carbon dioxide in the cathode exhaust fluid.

[0057] The flowmeter 62 is provided so as to follow the gas/liquid separator 52, for example, in the middle of the flow path P4. The flowmeter 62 can measure the flow rate of the processed anode exhaust fluid flowing through the flow path P4, for example. The flowmeter 62 can measure the total flow rate of gases such as oxygen and carbon dioxide in the anode exhaust fluid.

[0058] The power supply 70 can supply power to the electrochemical reaction structure 10, for example. The power supply 70 is connected to the current collector 16 and the current collector 17, for example. The power supply 70 can apply power to the electrochemical reaction structure 10 to cause an electrolytic reaction such as an oxidation reaction or a reduction reaction, and is electrically connected to the cathode 11 and the anode 12. The electric energy supplied by the power supply 70 is used to cause a reduction reaction at the cathode 11 and an oxidation reaction at the anode 12. The power supply 70 and the current collector 16 are connected by wiring and the power supply 70 and the current collector 17 are connected by wiring, for example. Between the electrochemical reaction structure 10 and the power supply 70, electric devices such as inverters, converters, and batteries may be installed as needed. The electrochemical reaction structure 10 may be driven by a constant-voltage system or a constant-current system.

[0059] The power supply 70 may be an ordinary commercial power supply, a battery, or the like, or may be a power supply that converts renewable energy to electric energy and supplies it. Examples of such a power supply include a power supply that converts kinetic energy or potential energy such as wind power, water power, geothermal power, or tidal power to electric energy, a power supply such as a solar cell including a photoelectric conversion element that converts light energy to electric energy, a power supply such as a fuel cell or a storage battery that converts chemical energy to electric energy, and a power supply such as an apparatus that converts vibrational energy such as sound to electric energy. The photoelectric conversion element has a function of performing charge separation by emitted light energy of sunlight or the like. Examples of the photoelectric conversion element include a pin-junction solar cell, a pn-junction solar cell, an amorphous silicon solar cell, a multijunction solar cell, a single crystal silicon solar cell, a polycrystalline silicon solar cell, a dye-sensitized solar cell, an organic thin-film solar cell, and so on. Further, the photoelectric conversion element may be stacked on at least one of the cathode 11 and the anode 12 inside the electrochemical reaction structure 10.

[0060] The power supply 70 can control the current or voltage to be supplied to the electrochemical reaction structure 10, for example. The power supply 70 may include a power controller that controls the current or voltage to be supplied to the electrochemical reaction structure 10, for example. The power supply 70 may have a function of controlling the pressure in the cathode chamber 140 or the pressure in the anode chamber 150 by controlling the current or voltage to be supplied to the electrochemical reaction structure 10 based on a control signal from the control device 80.

[0061] FIG. 3 is a schematic view illustrating another example configuration of the electrochemical reaction device in the arrangement. As illustrated in FIG. 3, the electrochemical reaction device 1 may further include a flow path P7 and a pump 90. The flow path P7 connects the gas/liquid separator 52 and the flow path P2 or the anode solution supply source, for example. The pump 90 is provided in the middle of the flow path P7. The gas/liquid separator 52 separates the anode exhaust fluid into a liquid component such as the second electrolytic solution and a gas component such as oxygen, hydrogen, and carbon dioxide and the pump 90 returns the liquid component to the flow path P2 through the flow path P7, thereby enabling circulation of the anode solution. The flow paths P1, P2, P3, P4, P5, P6, and P7 can be formed using pipes, for example.

[0062] FIG. 4 is a schematic view illustrating another example configuration of the electrochemical reaction device in the arrangement. As illustrated in FIG. 4, the electrochemical reaction device 1 may further include a temperature controller 71. The temperature controller 71 is directly or indirectly connected to the electrochemical reaction structure 10. The temperature controller 71 can measure and control, for example, the temperature (for example, external temperature) of the electrochemical reaction structure 10. The temperature controller 71 may include a heater capable of heating the electrochemical reaction structure 10 or a cooler capable of cooling the electrochemical reaction structure 10. The temperature controller 71 may measure at least one of the temperatures of the cathode chamber 140 and the anode chamber 150 and control these temperatures. The temperature controller 71 may have a function of controlling the pressure in the cathode chamber 140 and the pressure in the anode chamber 150 by controlling at least one of the temperature of the electrochemical reaction structure 10, the temperature of the cathode chamber 140, and the temperature of the anode chamber 150 based on a control signal from the control device 80.

[0063] The control device 80 is connected to at least one of the controllers of the flow rate controller 21, the flow rate

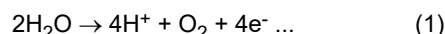
controller 22, the pressure controller 41, the pressure controller 42, the temperature controller 71, and the power supply 70, for example, by a wired connection or a wireless connection. For example, as illustrated in FIG. 1, the control device 80 is connected to each of the flow rate controller 21, the flowmeter 61, and the flowmeter 62 by a wired connection or a wireless connection. The control device 80 can, for example, measure the sum of the flow rate of the cathode supply fluid flowing through the flow path P1, the flow rate of the processed cathode exhaust fluid flowing through the flow path P3, and the flow rate of the processed anode exhaust fluid flowing through the flow path P4, and control the operating conditions of the electrochemical reaction structure 10 according to the measured sum value. The control device 80 may control a pressure difference (differential pressure) between the cathode chamber 140 and the anode chamber 150, for example, by controlling at least one of the controllers of the flow rate controller 21, the flow rate controller 22, the pressure controller 41, the pressure controller 42, the temperature controller 71, and the power supply 70 according to the measured sum value, for example.

[0064] The control device 80 includes hardware including an arithmetic device such as a processor, for example. Each operation may be stored as an operation program in a computer-readable recording medium such as a memory, and each operation may be executed by appropriately reading the operation program stored in the recording medium by hardware.

[0065] FIG. 5 is a schematic view illustrating another example configuration of the electrochemical reaction device in the arrangement. As illustrated in FIG. 5, the control device 80 may be further connected to at least one of the pressure controller 41 and the pressure controller 42 by a wired connection or a wireless connection. The control device 80 can, for example, measure the sum of the flow rate of the cathode supply fluid flowing through the flow path P1, the flow rate of the processed cathode exhaust fluid flowing through the flow path P3, and the flow rate of the processed anode exhaust fluid flowing through the flow path P4 and control at least one of the pressure controller 41 and the pressure controller 42 according to the measured sum value to control the operating conditions of the electrochemical reaction structure 10.

[0066] FIG. 6 is a schematic view illustrating another example configuration of the electrochemical reaction device in the arrangement. As illustrated in FIG. 6, the control device 80 may be connected to at least one of the pressure controller 41 and the pressure controller 42 by a wired connection or a wireless connection, and does not need to be connected to the flow rate controller 22. The control device 80 can, for example, measure the sum of the flow rate of the cathode supply fluid flowing through the flow path P1, the flow rate of the processed cathode exhaust fluid flowing through the flow path P3, and the flow rate of the processed anode exhaust fluid flowing through the flow path P4 and control at least one of the pressure controller 41 and the pressure controller 42 according to the measured sum value to control the operating conditions of the electrochemical reaction structure 10. The configurations illustrated in FIGs. 1, 2, 3, 4, 5, and 6 may be combined as appropriate.

[0067] Next, there is explained an example method of operating the electrochemical reaction device 1. Here, there is explained the case where carbon dioxide is reduced to produce carbon monoxide mainly and water is oxidized to produce oxygen. When the cathode supply fluid containing carbon dioxide is supplied to the cathode chamber 140, the anode supply fluid containing the second electrolytic solution is supplied to the anode chamber 150, and a voltage that is equal to or more than the electrolysis voltage is applied between the cathode 11 and the anode 12 by supplying power by the power supply 70, the oxidation reaction of water occurs near the anode 12 in contact with the second electrolytic solution. As expressed in the following expression (1), an oxidation reaction of water contained in the second electrolytic solution occurs, electrons are lost, and oxygen and hydrogen ions are produced. Some of the produced hydrogen ions move to the cathode chamber 140 through the diaphragm 13.



[0068] When the hydrogen ions (H^+) produced on the anode 12 side reach the vicinity of the cathode 11 and at the same time, electrons (e^-) are supplied to the cathode 11 from the power supply 70, the reduction reaction of carbon dioxide occurs. As expressed in the following expression (2), carbon dioxide is reduced by the hydrogen ions (H^+) that have moved to the vicinity of the cathode 11 and the electrons (e^-) supplied from the power supply 70 to produce carbon monoxide.



[0069] The gas component contained in the anode exhaust fluid from the anode chamber 150 is mainly an oxygen gas, as expressed in The expression (1). In the reactions at the cathode 11 and the anode 12, most of the carbon dioxide contained in the cathode supply fluid supplied to the cathode chamber 140 is reduced at the cathode 11, but some flows to the anode 12 side as carbon dioxide or as ions such as carbonate ions (CO_3^{2-}) or hydrogen carbonate ions (HCO_3^-). The carbonate ions or the hydrogen carbonate ions that have moved to the anode 12 side become present as carbon dioxide by a chemical equilibrium reaction when the pH of the anode solution (second electrolytic solution) becomes, for example, six or less, and some of the carbon dioxide is dissolved in the anode solution. Such a carbon dioxide gas, which is not fully dissolved in the anode solution, is contained with the oxygen gas in the anode exhaust fluid discharged from the anode chamber 150. Under general operating conditions of the electrochemical reaction structure 10, the abundance ratio of the

carbon dioxide gas to the oxygen gas in the anode exhaust fluid increases up to, for example, 2: 1 in some cases.

[0070] The electrochemical reaction device in the arrangement can predict the state of the electrochemical reaction of the electrochemical reaction structure 10 by understanding the flow rate of the cathode supply fluid flowing through the flow path P1, the flow rate of the cathode exhaust fluid flowing through the flow path P3 (cathode exhaust fluid processed by the dehydrator 51), and the flow rate of the anode exhaust fluid flowing through the flow path P4 (anode exhaust fluid processed by the gas/liquid separator 52). Through the reaction represented by the expression (2), carbon dioxide is consumed at the cathode 11, but an equal amount of carbon compound (carbon monoxide, here) is produced. Furthermore, the same amount of carbon dioxide as the amount of carbon compound produced moves toward the anode 12. When the flow rate of the carbon dioxide gas in the cathode supply fluid flowing through the flow path P1 is assumed to 100 and the current having a theoretical amount necessary to reduce the carbon dioxide gas whose flow rate is assumed to 50 is supplied from the power supply 70 to the electrochemical reaction structure 10, the ratios of carbon dioxide, carbon monoxide, and hydrogen in the case of the Faraday efficiency (FE) being 100%, 90%, 70%, and 50% are as illustrated in Table 1, for example. Data indicating such a relationship are registered (recorded) in the control device 80 in advance, and the difference between the registered data and the actual measured data and changes in the operating situation over time are checked, thereby making it possible to understand the operating status.

[Table 1]

	FE	100%	90%	70%	50%
Cathode exhaust fluid	CO ₂	0	10	30	50
	CO	50	45	35	25
	H ₂	0	5	15	25
	Subtotal	50	60	80	100
Anode exhaust fluid	CO ₂	50	45	35	25
	O ₂	25	25	25	25
	Subtotal	75	70	60	50
Total		125	130	140	150

[0071] When a hydrogen production reaction, which is a side reaction, proceeds due to catalyst deterioration or a phenomenon such as flooding in which the cathode catalyst is covered with water or an electrolytic solution, a change in the cathode exhaust fluid occurs such that the Faraday efficiency illustrated in Table 1 decreases from 100% to 90% or 70%. When carbon dioxide whose flow rate is assumed to 100 flows through the flow path P3 and the Faraday efficiency decreases, the sum of the flow rate of the processed cathode exhaust fluid flowing through the flow path P3 and the flow rate of the processed anode exhaust fluid flowing through the flow path P4 increases to 125 when the Faraday efficiency is 100%, increases to 130 when the Faraday efficiency is 90%, and increases to 140 when the Faraday efficiency is 100%. Thus, for example, by measuring the sum of the flow rate of the cathode supply fluid flowing through the flow path P1, the flow rate of the processed cathode exhaust fluid flowing through the flow path P3, and the flow rate of the processed anode exhaust fluid flowing through the flow path P4, the decrease in Faraday efficiency can be checked. Further, by comparing the actual measured data of the sum with the registered data in the control device 80, the deterioration over a long-term operation can be understood.

[0072] The decrease in Faraday efficiency due to deterioration over a long-term operation causes, for example, a failure mode called cross leak in which a gaseous substance moves to one of the cathode 11 side and the anode 12 side, or to each other. When a reduction product moves from the cathode 11 side to the anode 12 side, a carbon compound or hydrogen produced at the cathode 11 is oxidized at the anode 12 and converted into carbon dioxide or water. When hydrogen is produced, the sum of the flow rate of the processed cathode exhaust fluid flowing through the flow path P3 and the flow rate of the processed anode exhaust fluid flowing through the flow path P4 decreases because hydrogen molecules are small, the cross leak of hydrogen moving through the diaphragm 13 increases, and the product is converted from gas into liquid due to conversion of hydrogen into water at the anode 12. The respective variations in the flow rates of the processed cathode exhaust fluid and the processed anode exhaust fluid when hydrogen is converted into water are illustrated in Table 2. When the Faraday efficiency decreases to 90% due to the cross leak, the sum of the flow rate of the processed cathode exhaust fluid flowing through the flow path P3 and the flow rate of the processed anode exhaust fluid flowing through the flow path P4 decreases from 130 to 125. This variation can be used to detect the increase or decrease in cross leak during a long-term operation and control operation.

[Table 2]

	FE	90%	70%	50%
Cathode exhaust fluid	CO ₂	10	30	50
	CO	45	35	25
	H ₂	0	0	0
	Subtotal	55	65	75
Anode exhaust fluid	CO ₂	45	35	25
	O ₂	25	25	25
	Subtotal	70	60	50
Total		125	125	125

[0073] For example, when operation is performed with the Faraday efficiency being 90%, the flow rate of the processed cathode exhaust fluid flowing through the flow path P3 varies from 60 in Table 1 to 55 in Table 2 over a long-term operation, and when the flow rate of the processed anode exhaust fluid flowing through the flow path P4 does not vary from 70 in Table 1 and remains 70 in Table 2, such a variation in the cathode exhaust fluid as illustrated in Table 2 caused by the occurrence of the cross leak can be detected and the operating conditions of each component can be controlled based on a control signal from the control device 80.

[0074] A known example of a conventional electrochemical reaction device, detects the total flow rate of fluid discharged from a cathode chamber or an anode chamber and to control the flow rate of a carbon dioxide gas in fluid supplied to the cathode chamber for controlling carbon dioxide contained in the fluid discharged from the cathode chamber according to a detection result. However, in order to detect changes in electrolysis performance such as a cross leak or deterioration caused by a long-term operation of the electrochemical reaction device, it is necessary to detect variations in the sum of the flow rate of the cathode supply fluid flowing through the flow path P1, the flow rate of the processed cathode exhaust fluid flowing through the flow path P3, and the flow rate of the processed anode exhaust fluid flowing through the flow path P4, as in the electrochemical reaction device in the arrangement.

[0075] The cathode chamber 140 and the anode chamber 150 has an appropriate balanced pressure therebetween, the appropriate balanced pressure can be set by controlling the pressures of cathode chamber 140 and the anode chamber 150 using, for example, the pressure controller 41 and the pressure controller 42. When the pressure in the cathode chamber 140 is low, water or an electrolytic solution may flow into the cathode 11 from the flow path P2. When too much water or electrolytic solution flows into the cathode 11, flooding occurs and the hydrogen production reaction, which is a side reaction, proceeds. When the pressure in the cathode chamber 140 is high, water or an electrolytic solution is not sufficiently supplied to the cathode 11, resulting in a problem that ion diffusion is inhibited. The pressure in the cathode chamber 140 is preferably controlled to a range of 0 PaG or more and 300 KPaG or less in gauge pressure. The pressure in the cathode chamber 140 can be controlled by the pressure controller 41, for example. The pressure in the cathode chamber 140 is more preferably controlled to 50 KPaG or more and 200 KPaG or less in gauge pressure. The pressure in the anode chamber 150 is preferably controlled to 0 PaG or more and 300 KPaG or less in gauge pressure. The pressure in the anode chamber 150 can be controlled by the pressure controller 42, for example. The pressure in the anode chamber 150 is more preferably controlled to 0 PaG or more and 200 KPaG or less in gauge pressure. The pressure difference (differential pressure) between the cathode chamber 140 and the anode chamber 150 is preferably controlled to 0 PaG or more and 150 KPaG or less in gauge pressure. The pressure in the cathode chamber 140 is preferably higher than that in the anode chamber 150. The control of the pressure difference between the cathode chamber 140 and the anode chamber 150 to the range, can reduce the hydrogen production reaction, which is a side reaction, for example.

[0076] When the control device 80 detects the occurrence of the cross leak from the cathode chamber 140 to the anode chamber 150, based on a control signal from the control device 80, at least one of the controllers of the flow rate controller 21, the flow rate controller 22, the pressure controller 41, the pressure controller 42, the power supply 70, and the temperature controller 71 is controlled, to thereby control the operating conditions of the electrochemical reaction structure 10. Further, the control device 80 may compare first data indicating the measured sum with second data registered in the control device 80 and control at least one of the controllers according to a comparison result, to thereby control the pressure difference. The control device 80 may analyze the variation in the measured sum over time and control at least one of the controllers according to an analysis result, to thereby control the pressure difference.

[0077] When the cross leak occurs, for example, the control device 80 controls the flow rate controller 21 to increase the flow rate of the cathode supply fluid flowing through the flow path P1, thereby making it possible to reduce the hydrogen production reaction.

[0078] When the hydrogen production reaction increases due to temperature rise and the cross leak occurs, the control

device 80 controls the flow rate controller 22 to increase the flow rate of the anode supply fluid flowing through the flow path P2, thereby making it possible to reduce increasing the temperature of the electrochemical reaction structure 10 to reduce the hydrogen production reaction.

[0079] When the variation in the pressure of the cathode chamber 140 or the pressure in the anode chamber 150 causes an increase in water inflow from the anode 12 side to the cathode 11 and the cross leak occurs, the control device 80 controls the pressure controller 41 to control the pressure in the cathode chamber 140 and controls the pressure controller 42 to control the pressure in the anode chamber 150, thereby making it possible to reduce electrolyzing water. Further, the control device 80 controls the power supply 70 to reduce the value of current or voltage to be supplied to the electrochemical reaction structure 10, thereby making it possible to prevent increasing the temperature of the electrochemical reaction structure 10 to reduce the hydrogen production reaction.

[0080] When the cross leak occurs, the control device 80 controls the heater of the temperature controller 71 to reduce the temperature of the electrochemical reaction structure 10, thereby making it possible to reduce the hydrogen production reaction.

[0081] The flow path P3 may be connected to a valuable material production device. Examples of the valuable material production device include a chemical synthesis device that produces valuable materials through chemical synthesis using raw materials such as carbon monoxide, and so on. Examples of the valuable material include methanol produced by a methanol production device, hydrocarbons produced by a Fischer-Tropsch reactor, synthetic gasoline, light oil, jet fuel, olefin compounds produced by an olefin production device, and so on. The valuable material production device provided so as to follow the electrochemical reaction structure 10, can produce valuable materials having a high added value from the product of the electrochemical reaction structure 10.

[0082] The type of the chemical synthesis device is not particularly limited as long as it is capable of causing a reaction to synthesize another substance from the reduction product produced at the cathode 11. Examples of the reaction using the reduction product by the chemical synthesis device, include a chemical reaction, an electrochemical reaction, biological conversion reactions using products such as algae, enzyme, yeast, and bacteria, and so on.

[0083] The flow path P3 may be connected to a product separator instead of to the valuable material production device. The product separator can separate a carbon compound such as carbon monoxide, which is a product, by separating excess carbon dioxide from the cathode exhaust fluid or removing water from the cathode exhaust fluid. For example, when the carbon monoxide gas is produced in the electrochemical reaction structure 10 by the expression (2), by using, as a raw material, a mixed gas containing the produced carbon monoxide gas and a hydrogen gas as a byproduct of the reduction reaction, methanol can be produced through methanol synthesis, or jet fuel, light oil, or the like can be produced through Fischer-Tropsch synthesis. The present invention is not limited to this, and the flow path P3 may be connected to a tank that stores gas containing carbon compounds such as carbon monoxide instead of to the valuable material production device.

[0084] The reduction product may contain hydrogen obtained by electrolysis of carbon dioxide, carbon monoxide, and water. The concentration of hydrogen can be arbitrarily controlled depending on uses. In the case where hydrogen is used in the chemical synthesis device, carbon dioxide may be separated from the cathode exhaust fluid to be used, in order to use the mixture of carbon monoxide and hydrogen. In the case where hydrogen is not used, carbon monoxide is only separated from the cathode exhaust fluid. In the case where methanol is produced, by controlling the number of moles of hydrogen to about twice the number of moles of carbon monoxide, the hydrogen produced at the cathode 11 can be used as a valuable material. In the meantime, at the cathode 11, the side reaction of hydrogen can be inhibited depending on the reaction conditions to control the concentration of hydrogen in the reduction product to a range of 0.1% or more and 5% or less in volume percent. This makes it possible to use the electrochemical reaction device as a carbon monoxide production device that produces high-concentration carbon monoxide.

[0085] The configurations in the arrangements are applicable in combination, and parts thereof are also replaceable. 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 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 inventions.

[0086] The arrangements can be summarized into the following clauses.

(Clause 1) An electrochemical reaction device comprising:

an electrochemical reaction structure comprising:

a cathode having a reduction catalyst that promotes a reduction reaction of reducing carbon dioxide to produce a carbon compound;

an anode having an oxidation catalyst that promotes an oxidation reaction of oxidizing water to produce

oxygen;
 a diaphragm between the cathode and the anode,
 a cathode chamber facing on the cathode; and
 an anode chamber facing on the anode;

a first flow path through which a first fluid flows, the first flow path being connected to an inlet of the cathode chamber, and the first fluid being supplied to the cathode chamber and containing the carbon dioxide;
 a second flow path through which a second fluid flows, the second flow path being connected to an inlet of the anode chamber, the second fluid being supplied to the anode chamber and containing the water;
 a third flow path through which a third fluid flows, the third flow path being connected to an outlet of the cathode chamber, and the third fluid being discharged from the cathode chamber and containing the carbon compound;
 a fourth flow path through which a fourth fluid flows, the fourth flow path being connected to an outlet of the anode chamber, and the fourth fluid being discharged from the anode chamber and containing the water and the oxygen;
 at least one controller selected from the group consisting of a first flow rate controller, a second flow rate controller, a first pressure controller, a second pressure controller, a temperature controller and a power supply, the first flow rate controller being configured to control a flow rate of the first fluid flowing through the first flow path, the second flow rate controller being configured to control a flow rate of the second fluid flowing through the second flow path, the first pressure controller being configured to control a pressure of the third flow path, the second pressure controller being configured to control a pressure of the fourth flow path, the temperature controller being configured to control a temperature of the electrochemical reaction structure, the power supply being configured to control a current or a voltage to be supplied to the electrochemical reaction structure, and the at least one controller including the first flow rate controller;
 a gas/liquid separator provided in the middle of the fourth flow path and configured to process the fourth fluid to separate a liquid containing the water from the fourth fluid;
 a first flowmeter configured to measure a flow rate of the third fluid flowing through the third flow path;
 a second flowmeter configured to measure a flow rate of the processed fourth fluid flowing through the fourth flow path; and
 a control device connected to the at least one controller, the first flowmeter and the second flowmeter, the control device being configured to measure a sum of the flow rate of the first fluid flowing through the first flow path, the flow rate of the third fluid flowing through the third flow path, and the flow rate of the processed fourth fluid flowing through the fourth flow path, and being configured to control the at least one controller according to the sum to control a pressure difference between the cathode chamber and the anode chamber.

(Clause 2) The electrochemical reaction device according to clause 1, further comprising:

a humidifier provided in the middle of the first flow path and configured to humidify carbon dioxide in the first fluid.

(Clause 3) The electrochemical reaction device according to claim 1 or claim 2, further comprising:

a dehydrator provided in the middle of the third flow path so as to precede the first flowmeter, and configured to process the third fluid to separate the water from the third fluid.

(Clause 4) The electrochemical reaction device according to any one of the clause 1 to the clause 3, wherein

the control device is configured to control the first flow rate controller according to the sum, and is configured to control the flow rate of the first fluid flowing through the first flow path to control the pressure difference.

(Clause 5) The electrochemical reaction device according to any one of the clause 1 to the clause 4, wherein the at least one controller includes:

the first pressure controller; and

the second pressure controller, and

the control device is configured to control the first pressure controller according to the sum to control the pressure of the third flow path, and to control the second pressure controller according to the sum to control the pressure of the fourth flow path, and thus control the pressure difference.

(Clause 6) The electrochemical reaction device according to any one of the clause 1 to the clause 5, wherein

the at least one controller includes the second flow rate controller, and

the control device is configured to control the second flow rate controller according to the sum, and is configured to control the flow rate of the second fluid flowing through the second flow path to control the pressure difference.

(Clause 7) The electrochemical reaction device according to any one of the clause 1 to the clause 6, wherein

the at least one controller includes the temperature controller, and
the control device is configured to control the temperature controller according to the sum, and is configured to
control the temperature of the electrochemical reaction structure to control the pressure difference.

(Clause 8) The electrochemical reaction device according to the clause 7, wherein
the temperature controller includes a heater configured to heat the electrochemical reaction structure.
(Clause 9) The electrochemical reaction device according to any one of the clause 1 to the clause 8, wherein

the at least one controller includes the power supply, and
the control device is configured to control the power supply according to the sum, and is configured to control the
current or the voltage to be supplied to the electrochemical reaction structure to control the pressure difference.

(Clause 10) The electrochemical reaction device according to any one of the clause 1 to the clause 9, wherein
the control device is configured to compare a first data indicating the sum with a second data to be stored in the control
device, and is configured to control the at least one controller according to a comparison result to control the pressure
difference.

(Clause 11) The electrochemical reaction device according to any one of the clause 1 to the clause 10, wherein
the control device is configured to analyze variations in the sum over time, and is configured to control the at least one
controller according to a result of the analyzation to control the pressure difference.

(Clause 12) A method of operating an electrochemical reaction device,

the electrochemical reaction device comprising an electrochemical reaction structure,
the electrochemical reaction structure comprising:

a cathode having a reduction catalyst that promotes a reduction reaction of reducing carbon dioxide to
produce a carbon compound;
an anode having an oxidation catalyst that promotes an oxidation reaction of oxidizing water to produce
oxygen;
a diaphragm between the cathode and the anode,
a cathode chamber facing on the cathode; and
an anode chamber facing on the anode;

a first flow path through which a first fluid flows, the first flow path being connected to an inlet of the cathode
chamber, and the first fluid being supplied to the cathode chamber and containing the carbon dioxide;
a second flow path through which a second fluid flows, the second flow path being connected to an inlet of the
anode chamber, and the second fluid being supplied to the anode chamber and containing the water;
a third flow path through which a third fluid flows, the third flow path being connected to an outlet of the cathode
chamber, and the third fluid being discharged from the cathode chamber and containing the produced carbon
compound;

a fourth flow path through which a fourth fluid flows, the fourth flow path being connected to an outlet of the anode
chamber, and the fourth fluid being discharged from the anode chamber and containing the water and the
produced oxygen;

at least one controller selected from the group consisting of a first flow rate controller, a second flow rate controller,
a first pressure controller, a second pressure controller, a temperature controller and a power supply, the first flow
rate controller being configured to control a flow rate of the first fluid flowing through the first flow path, the second
flow rate controller being configured to control a flow rate of the second fluid flowing through the second flow path,
the first pressure controller being configured to control a pressure of the third flow path, the second pressure
controller being configured to control a pressure of the fourth flow path, the temperature controller being
configured to control a temperature of the electrochemical reaction structure, the power supply being configured
to control a current or a voltage to be supplied to the electrochemical reaction structure, and the at least one
controller including the first flow rate controller;

a gas/liquid separator provided in the middle of the fourth flow path and configured to process the fourth fluid to
separate a liquid containing the water from the fourth fluid;

a first flowmeter configured to measure a flow rate of the third fluid flowing through the third flow path; and
a second flowmeter configured to measure a flow rate of the processed fourth fluid flowing through the fourth flow
path,

the method comprising:

supplying the first fluid to the cathode chamber, supplying the second fluid to the anode chamber, and supplying a current or a voltage to the electrochemical reaction structure, to reduce the carbon dioxide by the cathode to produce the carbon compound and to reduce the water by the anode to produce the oxygen; and measuring the sum of the flow rate of the first fluid flowing through the first flow path, the flow rate of the third fluid flowing through the third flow path, and the flow rate of the processed fourth fluid flowing through the fourth flow path and controlling the at least one controller according to the sum to control a pressure difference between the cathode chamber and the anode chamber.

(Clause 13) The method according to the clause 12, wherein

a pressure in the cathode chamber is controlled to a range of 0 PaG or more and 300 KPaG or less, a pressure in the anode chamber is controlled to 0 PaG or more and 300 KPaG or less, the pressure difference is controlled to 0 PaG or more and 150 KPaG or less, and the pressure in the cathode chamber is higher than the pressure in the anode chamber.

(Clause 14) The method according to clause 12, wherein

the electrochemical reaction device further comprises at least one selected from the group consisting of a humidifier and a dehydrator, the humidifier is provided in the middle of the flow path and is configured to humidify carbon dioxide in the first fluid, and the dehydrator is provided in the middle of the third flow path so as to precede the first flowmeter and is configured to process the third fluid to separate the water from the third fluid.

(Clause 15) The method according to clause 12, wherein

the electrochemical reaction device further comprises a control device, and the control device is configured to control the first flow rate controller according to the sum and is configured to control the flow rate of the first fluid flowing through the first flow path to control the pressure difference.

(Clause 16) The method according to clause 12, wherein

the electrochemical reaction device further comprises a control device, the at least one controller includes:

the first pressure controller; and the second pressure controller, and the control device is configured to control the first pressure controller according to the sum to control the pressure of the third flow path and controls the second pressure controller according to the sum to control the pressure of the fourth flow path, and thereby controls the pressure difference.

(Clause 17) The method according to clause 12, wherein

the electrochemical reaction device further comprises a control device, the at least one controller includes the second flow rate controller, and the control device is configured to control the second flow rate controller according to the sum, and is configured to control the flow rate of the second fluid flowing through the second flow path to control the pressure difference.

(Clause 18) The method according to any one of clause 12 to clause 17, wherein

the electrochemical reaction device further comprises a control device, the at least one controller includes the temperature controller, and the control device is configured to control the temperature controller according to the sum, and is configured to control the temperature of the electrochemical reaction structure to control the pressure difference.

(Clause 19) The electrochemical reaction device according to any one of clause 12 to clause 17, wherein

the electrochemical reaction device further comprises a control device,

the at least one controller includes the power supply, and
the control device is configured to control the power supply according to the sum, and is configured to control the
current or the voltage to be supplied to the electrochemical reaction structure to control the pressure difference.

(Clause 20) The method according to clause 12, wherein

the electrochemical reaction device further includes a control device, and
the control device is configured to compare a first data indicating the sum with a second data to be stored in the
control device, and is configured to control the at least one controller according to a comparison result to control
the pressure difference, or
the control device is configured to analyze variations in the sum over time, and is configured to control the at least
one controller according to a result of the analyzation to control the pressure difference.

Claims

1. An electrochemical reaction device comprising:

an electrochemical reaction structure comprising:

a cathode having a reduction catalyst that promotes a reduction reaction of reducing carbon dioxide to
produce a carbon compound;
an anode having an oxidation catalyst that promotes an oxidation reaction of oxidizing water to produce
oxygen;
a diaphragm between the cathode and the anode,
a cathode chamber facing on the cathode; and
an anode chamber facing on the anode;

a first flow path through which a first fluid flows, the first flow path being connected to an inlet of the cathode
chamber, and the first fluid being supplied to the cathode chamber and containing the carbon dioxide;
a second flow path through which a second fluid flows, the second flow path being connected to an inlet of the
anode chamber, the second fluid being supplied to the anode chamber and containing the water;
a third flow path through which a third fluid flows, the third flow path being connected to an outlet of the cathode
chamber, and the third fluid being discharged from the cathode chamber and containing the carbon compound;
a fourth flow path through which a fourth fluid flows, the fourth flow path being connected to an outlet of the anode
chamber, and the fourth fluid being discharged from the anode chamber and containing the water and the oxygen;
at least one controller selected from the group consisting of a first flow rate controller, a second flow rate controller,
a first pressure controller, a second pressure controller, a temperature controller and a power supply, the first flow
rate controller being configured to control a flow rate of the first fluid flowing through the first flow path, the second
flow rate controller being configured to control a flow rate of the second fluid flowing through the second flow path,
the first pressure controller being configured to control a pressure of the third flow path, the second pressure
controller being configured to control a pressure of the fourth flow path, the temperature controller being
configured to control a temperature of the electrochemical reaction structure, the power supply being configured
to control a current or a voltage to be supplied to the electrochemical reaction structure, and the at least one
controller including the first flow rate controller;
a gas/liquid separator provided in the middle of the fourth flow path and configured to process the fourth fluid to
separate a liquid containing the water from the fourth fluid;
a first flowmeter configured to measure a flow rate of the third fluid flowing through the third flow path;
a second flowmeter configured to measure a flow rate of the processed fourth fluid flowing through the fourth flow
path; and
a control device connected to the at least one controller, the first flowmeter and the second flowmeter, the control
device being configured to measure a sum of the flow rate of the first fluid flowing through the first flow path, the
flow rate of the third fluid flowing through the third flow path, and the flow rate of the processed fourth fluid flowing
through the fourth flow path, and being configured to control the at least one controller according to the sum to
control a pressure difference between the cathode chamber and the anode chamber.

2. The electrochemical reaction device according to claim 1, further comprising:

a humidifier provided in the middle of the first flow path and configured to humidify carbon dioxide in the first fluid.

3. The electrochemical reaction device according to claim 1 or claim 2, further comprising:
a dehydrator provided in the middle of the third flow path so as to precede the first flowmeter, and configured to process
the third fluid to separate the water from the third fluid.
- 5 4. The electrochemical reaction device according to any one of claim 1 to claim 3, wherein
the control device is configured to control the first flow rate controller according to the sum, and is configured to control
the flow rate of the first fluid flowing through the first flow path to control the pressure difference.
- 10 5. The electrochemical reaction device according to any one of claim 1 to claim 4, wherein
the at least one controller includes:

the first pressure controller; and
the second pressure controller, and
the control device is configured to control the first pressure controller according to the sum to control the pressure
15 of the third flow path, and to control the second pressure controller according to the sum to control the pressure of
the fourth flow path, and thus control the pressure difference.
6. The electrochemical reaction device according to any one of claim 1 to claim 5, wherein

20 the at least one controller includes the second flow rate controller, and
the control device is configured to control the second flow rate controller according to the sum, and is configured to
control the flow rate of the second fluid flowing through the second flow path to control the pressure difference.
- 25 7. The electrochemical reaction device according to any one of claim 1 to claim 6, wherein

the at least one controller includes the temperature controller, and
the control device is configured to control the temperature controller according to the sum, and is configured to
control the temperature of the electrochemical reaction structure to control the pressure difference.
- 30 8. The electrochemical reaction device according to claim 7, wherein
the temperature controller includes a heater configured to heat the electrochemical reaction structure.
9. The electrochemical reaction device according to any one of claim 1 to claim 8, wherein

35 the at least one controller includes the power supply, and
the control device is configured to control the power supply according to the sum, and is configured to control the
current or the voltage to be supplied to the electrochemical reaction structure to control the pressure difference.
- 40 10. The electrochemical reaction device according to any one of claim 1 to claim 9, wherein
the control device is configured to compare a first data indicating the sum with a second data to be stored in the control
device, and is configured to control the at least one controller according to a comparison result to control the pressure
difference.
- 45 11. The electrochemical reaction device according to any one of claim 1 to claim 10, wherein
the control device is configured to analyze variations in the sum over time, and is configured to control the at least one
controller according to a result of the analyzation to control the pressure difference.
12. A method of operating an electrochemical reaction device,

50 the electrochemical reaction device comprising an electrochemical reaction structure,
the electrochemical reaction structure comprising:

a cathode having a reduction catalyst that promotes a reduction reaction of reducing carbon dioxide to
produce a carbon compound;
55 an anode having an oxidation catalyst that promotes an oxidation reaction of oxidizing water to produce
oxygen;
a diaphragm between the cathode and the anode,
a cathode chamber facing on the cathode; and

an anode chamber facing on the anode;

a first flow path through which a first fluid flows, the first flow path being connected to an inlet of the cathode chamber, and the first fluid being supplied to the cathode chamber and containing the carbon dioxide;

a second flow path through which a second fluid flows, the second flow path being connected to an inlet of the anode chamber, and the second fluid being supplied to the anode chamber and containing the water;

a third flow path through which a third fluid flows, the third flow path being connected to an outlet of the cathode chamber, and the third fluid being discharged from the cathode chamber and containing the produced carbon compound;

a fourth flow path through which a fourth fluid flows, the fourth flow path being connected to an outlet of the anode chamber, and the fourth fluid being discharged from the anode chamber and containing the water and the produced oxygen;

at least one controller selected from the group consisting of a first flow rate controller, a second flow rate controller, a first pressure controller, a second pressure controller, a temperature controller and a power supply, the first flow rate controller being configured to control a flow rate of the first fluid flowing through the first flow path, the second flow rate controller being configured to control a flow rate of the second fluid flowing through the second flow path, the first pressure controller being configured to control a pressure of the third flow path, the second pressure controller being configured to control a pressure of the fourth flow path, the temperature controller being configured to control a temperature of the electrochemical reaction structure, the power supply being configured to control a current or a voltage to be supplied to the electrochemical reaction structure, and the at least one controller including the first flow rate controller;

a gas/liquid separator provided in the middle of the fourth flow path and configured to process the fourth fluid to separate a liquid containing the water from the fourth fluid;

a first flowmeter configured to measure a flow rate of the third fluid flowing through the third flow path; and

a second flowmeter configured to measure a flow rate of the processed fourth fluid flowing through the fourth flow path,

the method comprising:

supplying the first fluid to the cathode chamber, supplying the second fluid to the anode chamber, and supplying a current or a voltage to the electrochemical reaction structure, to reduce the carbon dioxide by the cathode to produce the carbon compound and to reduce the water by the anode to produce the oxygen; and measuring the sum of the flow rate of the first fluid flowing through the first flow path, the flow rate of the third fluid flowing through the third flow path, and the flow rate of the processed fourth fluid flowing through the fourth flow path and controlling the at least one controller according to the sum to control a pressure difference between the cathode chamber and the anode chamber.

13. The method according to claim 12, wherein

a pressure in the cathode chamber is controlled to a range of 0 PaG or more and 300 KPaG or less,

a pressure in the anode chamber is controlled to 0 PaG or more and 300 KPaG or less,

the pressure difference is controlled to 0 PaG or more and 150 KPaG or less, and

the pressure in the cathode chamber is higher than the pressure in the anode chamber.

14. The method according to claim 12, wherein

the electrochemical reaction device further comprises at least one selected from the group consisting of a humidifier and a dehydrator,

the humidifier is provided in the middle of the flow path and is configured to humidify carbon dioxide in the first fluid, and

the dehydrator is provided in the middle of the third flow path so as to precede the first flowmeter and is configured to process the third fluid to separate the water from the third fluid.

15. The method according to claim 12, wherein

the electrochemical reaction device further comprises a control device, and

the control device is configured to control the first flow rate controller according to the sum and is configured to control the flow rate of the first fluid flowing through the first flow path to control the pressure difference.

FIG. 1

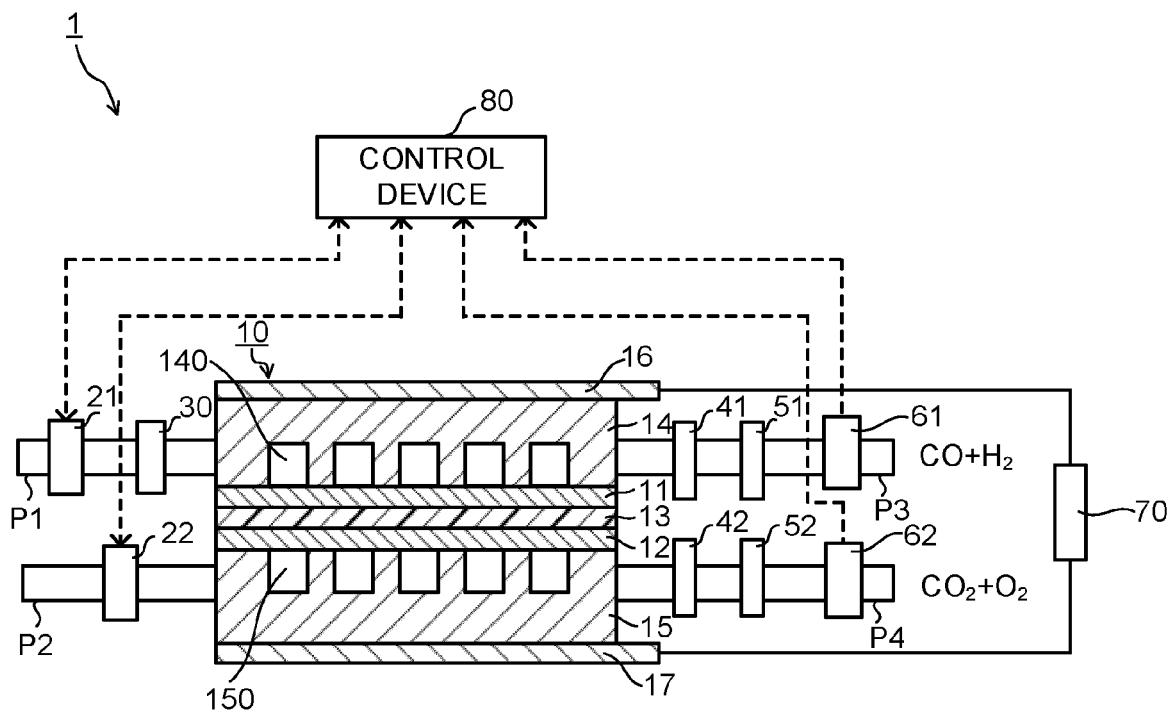


FIG. 2

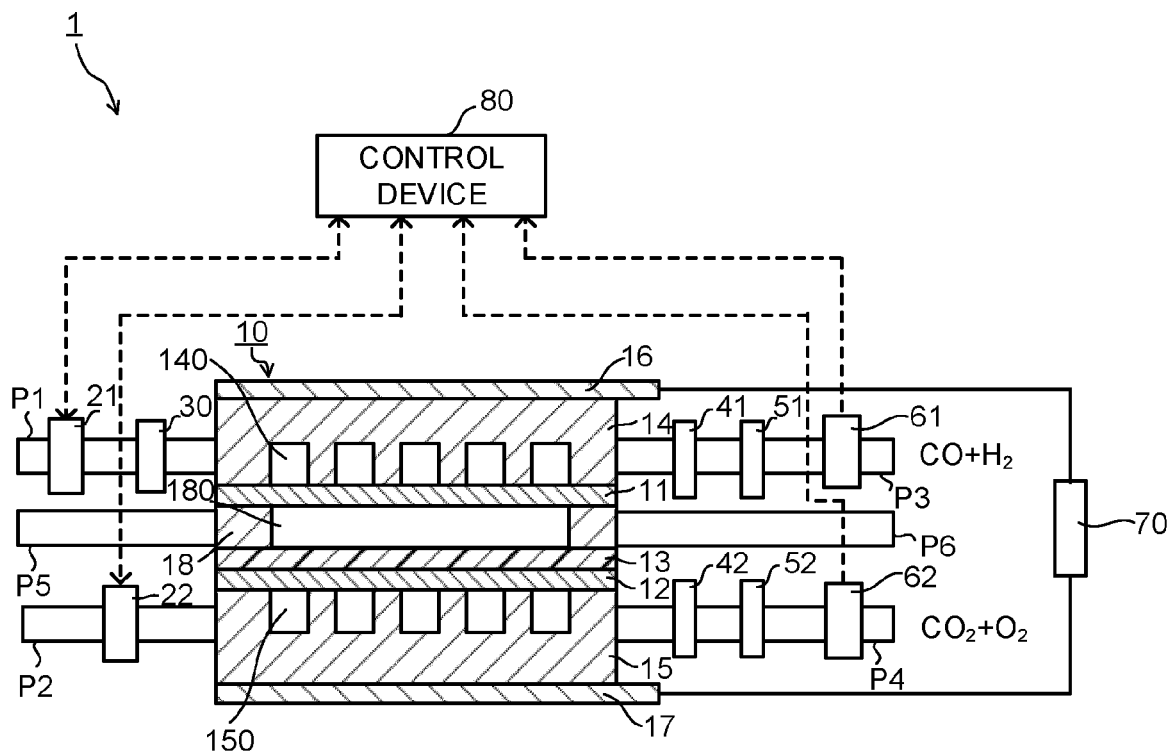


FIG. 3

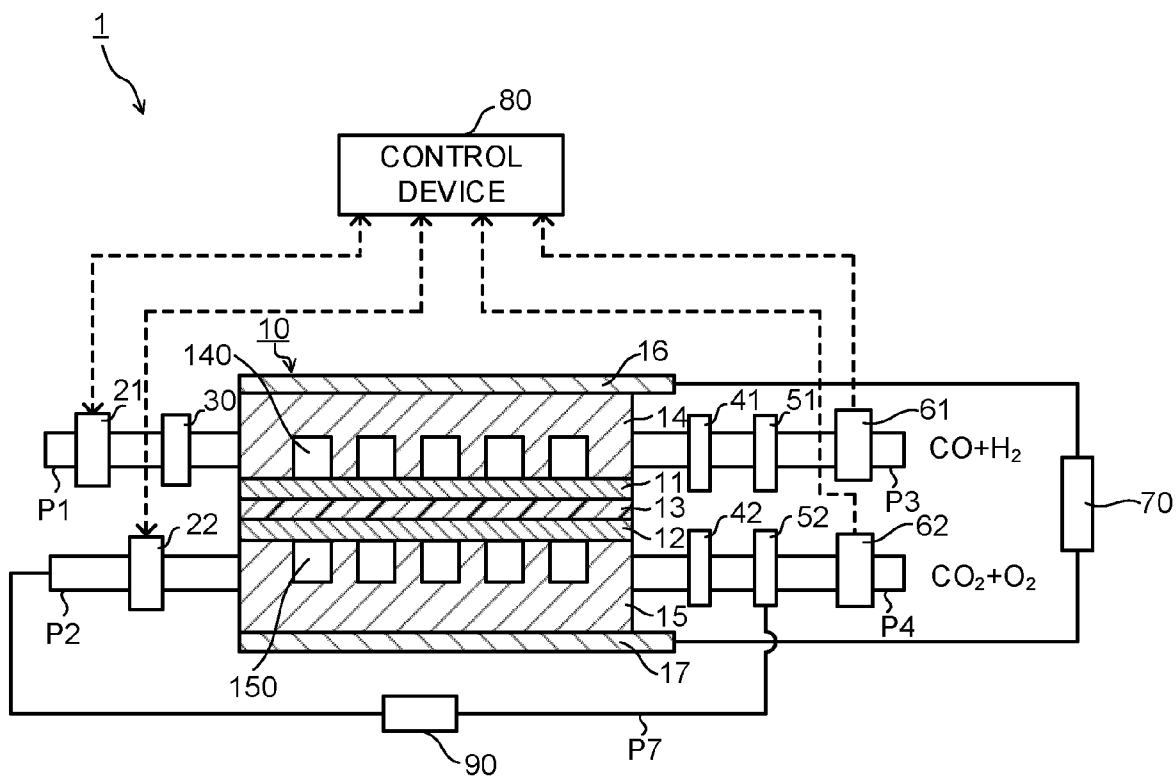


FIG. 4

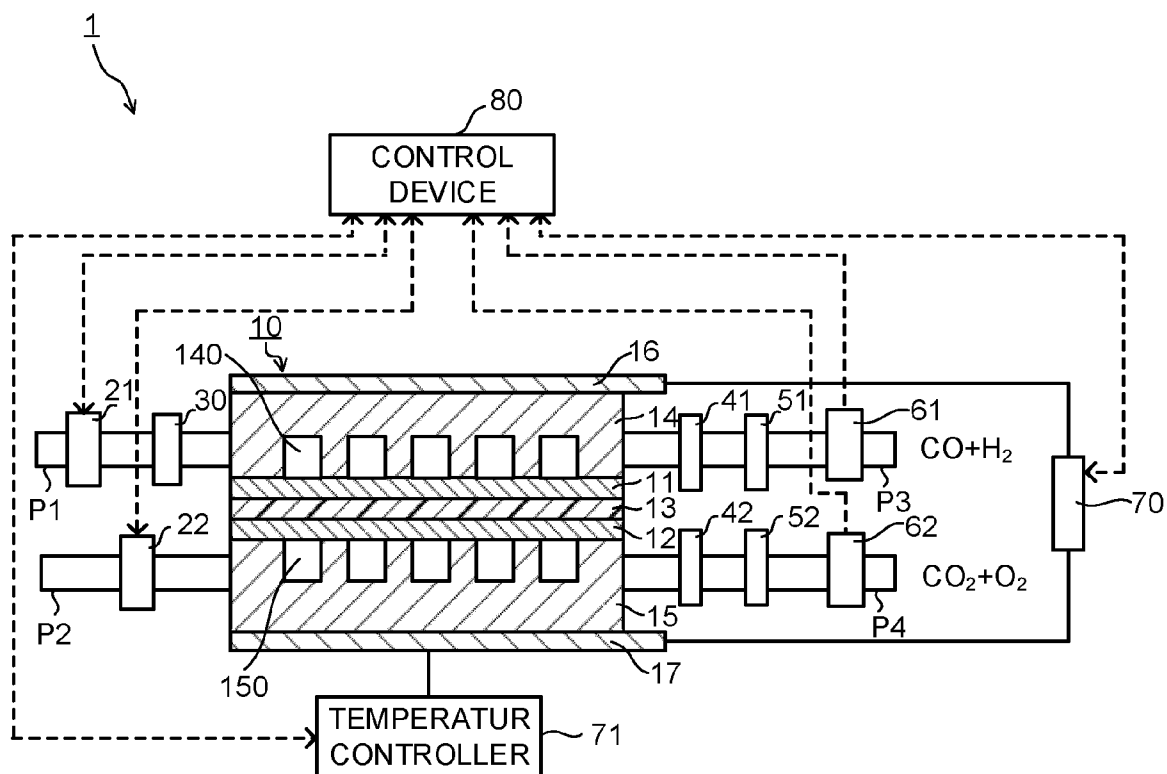


FIG. 5

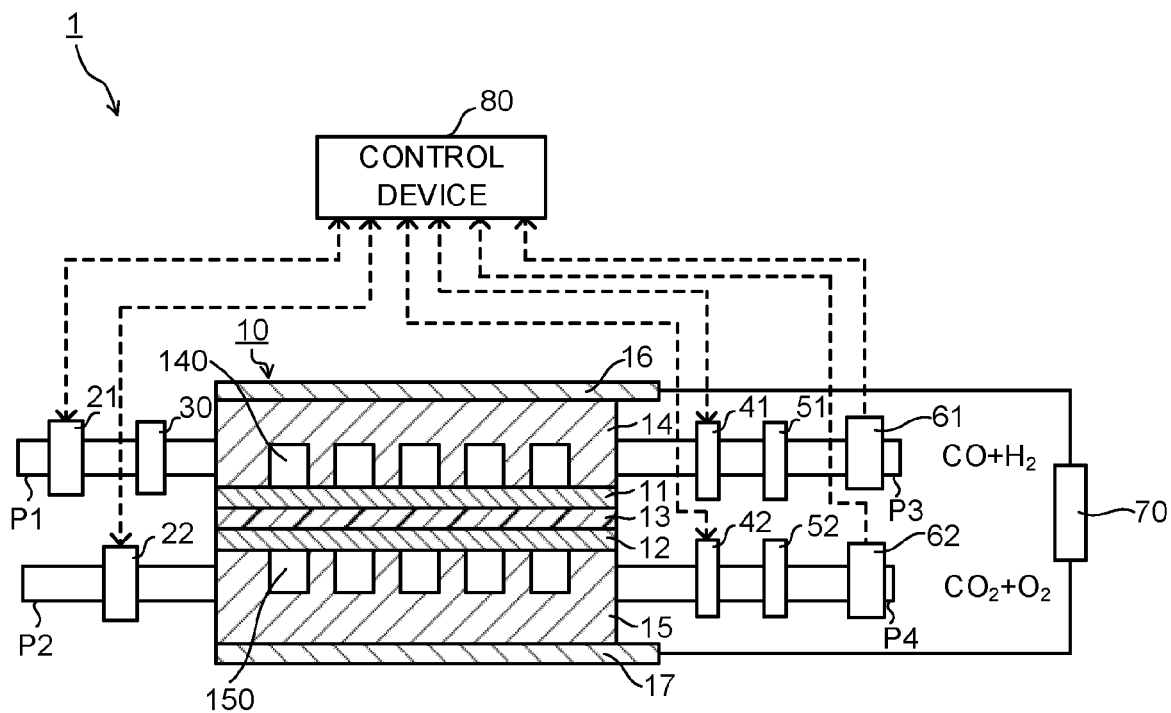
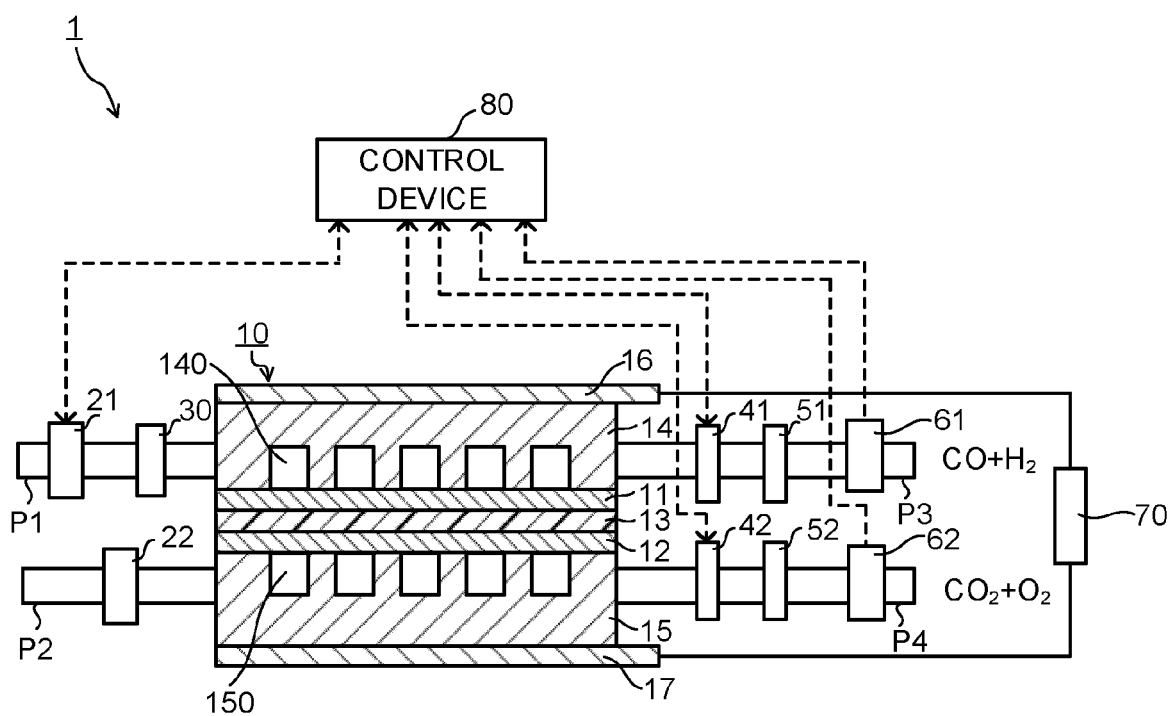


FIG. 6



REFERENCES CITED IN THE DESCRIPTION

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