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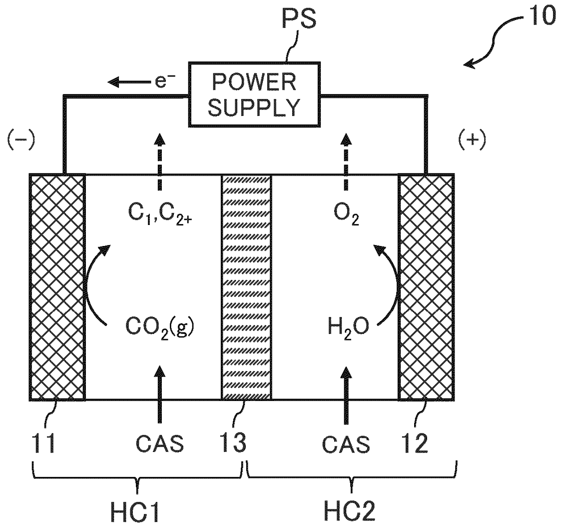
## (54) CARBON DIOXIDE RECYCLING SYSTEM

(57) The present invention provides a carbon dioxide recycling system that eliminates a need for a process that recovers and/or concentrates $CO_2$ to obtain a $CO_2$ gas at a high concentration and allows generating a $CO_2$ reduction product. The carbon dioxide recycling system according to the present invention includes: an electrochemical $CO_2$ reduction device that includes a reduction reaction electrode, an oxidation reaction electrode, and a first ion exchange membrane disposed between the reduction reaction electrode and the oxidation reaction electrode; and $CO_2$ gasification means that introduces a carbonate aqueous solution in which $CO_2$ is dissolved to a first half cell formed by including the reduction reaction electrode and the first ion exchange membrane as catholyte, and the $CO_2$ gasification means gasifying $CO_2$ in the catholyte immediately before reducing the $CO_2$ in the catholyte in the reduction reaction electrode.

FIG. 2



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## Description

### BACKGROUND

**[0001]** This invention relates to a carbon dioxide recycling system.

**[0002]** To solve an environmental problem, such as global warming, a reduction in an emission amount of carbon dioxide ($CO_2$) has been demanded. Additionally, expectations to a direct air capture (DAC) technique that artificially recovers $CO_2$ in the atmosphere and further a carbon dioxide capture and utilization (CCU) technique that reduces the recovered $CO_2$ to an effective chemical product for reuse have been increasing.

**[0003]** To achieve the $CO_2$ recycling and/or circulation system, using water (a proton source) and $CO_2$ (a carbon source) as raw materials, development of an artificial photosynthesis technique that synthesizes fuel and organic matters, such as hydrogen and hydrocarbon, has been advancing. Among the artificial photosynthesis techniques, an electrochemical $CO_2$ reduction device is a device that electrochemically reduces $CO_2$ under ordinary temperature and atmospheric pressure to produce an organic matter, such as a multicarbon compound. When the electrochemical $CO_2$ reduction device operates by renewable energy electric power, such as wind power generation and solar power generation, and the carbon source as the raw material recovered from $CO_2$ in the atmosphere is used, a carbon-negative $CO_2$ recycling device contributing to solution of an environmental problem and an energy problem is configured.

**[0004]** Fig. 11 illustrates one example of a conventional electrochemical $CO_2$ reduction device 200 described above. As illustrated in Fig. 11, the electrochemical $CO_2$ reduction device 200 includes a cathode chamber 201 as a half cell that reduces $CO_2$ and generates a carbon compound, an anode chamber 202 as a half cell that oxidizes water and generates oxygen, and an ion exchange membrane 203 that performs separation into the cathode chamber 201 and the anode chamber 202. In the device, as a cathode 204 disposed in the cathode chamber 201, for example, a cathode gas diffusion electrode (GDE) (a cathode GDE 204c) that includes a $CO_2$ reduction reaction catalyst (a cathode catalyst 204b) in a gas diffusion layer (GDL) with a micro porous layer (MPL) (a GDL 204a with an MPL) is used. As an anode 205 disposed in the anode chamber 202, for example, an anode GDE 205b that includes an oxygen evolution reaction (OER) catalyst (an OER catalyst 205a) is used. As the ion exchange membrane 203, an anion-exchange membrane (AEM) is used. For the cathode chamber 201 and the anode chamber 202, as electrolyte, a neutral to alkaline aqueous solution is used.

**[0005]** Here, when catholyte and anolyte are alkaline electrolyte, a $CO_2$ gas is dissolved (consumed) as carbonate. Since the AEM used in the alkaline environment transmits not only $OH^-$ but also carbonate ($HCO_3^-$, $CO_3^{2-}$), crossover occurs from the cathode 204 side to the anode 205 side, and even when a $CO_2$ gas is excessively supplied to the cathode 204, $CO_2$ usage proportion is considerably low. Therefore, the conventional device excessively supplies a $CO_2$ gas to satisfy a $CO_2$ reduction reaction in an alkaline environment. Even when the catholyte and the anolyte are neutral electrolyte, since $H_2O$ becomes a $H^+$ (a proton) source, alkalinization due to local generation of $OH^-$ and generation of carbonate in association with it cannot be avoided.

**[0006]** In the device, $CO_2$ as a carbon source of electrolytic reduction is supplied to the cathode catalyst 204b of the cathode GDE 204c as a $CO_2$ gas. The $CO_2$ reduction reaction in the cathode chamber 201 progresses with a three-phase interface between $CO_2$ (gas), aqueous electrolyte (liquid), and the cathode catalyst 204b (solid) as reaction fields. Therefore, to improve the usage proportion of $CO_2$ and further improve a generation speed of a $CO_2$ reduction product, $CO_2$ needs to be supplied as the gas on a catalyst (solid) surface in the electrolyte (liquid) as described above. As the $CO_2$ reduction product, a carbon compound ($C_1$, $C_{2+}$) with carbon number 1 or 2 or more is included. $C_1$,$C_{2+}$, and unreacted $CO_2$ generated by the electrochemical $CO_2$ reduction device 200 are discharged from the cathode GDE 204c. $O_2$ and the crossover $CO_2$ generated by the electrochemical $CO_2$ reduction device 200 is discharged from the anode GDE 205b. The crossover $CO_2$ means $CO_2$ generated by $CO_2$ supplied to the cathode 204 side passing through the ion exchange membrane 203 in the form of carbonate ($HCO_3^-$, $CO_3^{2-}$) to reach the anode 205 side and directly reacting to $H^+$ locally generated from $H_2O$ on the anode 205 side.

**[0007]** The conventional electrochemical $CO_2$ reduction device 200 supplies a $CO_2$ gas at a high concentration to the cathode chamber 201 of a $CO_2$ reduction cell. To improve the reaction efficiency, as described above, a device, such as application of the gas diffusion electrode (GDE), has been examined. In a place where the $CO_2$ gas at the high concentration cannot be ensured, since the $CO_2$ gas cannot be excessively suppled, the efficiency as the electrochemical $CO_2$ reduction device 200 lowers.

**[0008]** To ensure the $CO_2$ gas at the high concentration described above, a DAC process that recovers dilute $CO_2$ in the atmosphere and concentrates it is required. The current DAC process by a chemical adsorption method using an amine aqueous solution and a physical adsorption method by a porous solid adsorbent requires considerable energy for the concentration of $CO_2$ and considerable energy is taken for a process of desorbing $CO_2$ recovered from the atmosphere as a $CO_2$ gas again, and this becomes one factor of high cost.

**[0009]** As one example of the conventional electrochemical $CO_2$ reduction device, for example, there is a carbon dioxide reactor described in JP 2021-147679 A.

**[0010]** The carbon dioxide reactor includes an electrochemical reaction cell, a first supply unit, a second supply unit, and a first carbon dioxide separation unit. The above-described electrochemical reaction cell includes a first housing unit, a second housing unit, a diaphragm, a cathode, and an anode. The first housing unit houses first electrolyte containing a gas containing carbon dioxide, or carbon dioxide. The second housing unit houses second electrolyte containing water. The diaphragm is disposed between the first housing unit and the second housing unit. The cathode is disposed so as to be in contact with the gas or the first electrolyte, reduces the carbon dioxide, and generates a carbon compound. The anode is disposed so as to be in contact with the second electrolyte, oxidizes water, and generates oxygen. The first supply unit supplies the first housing unit with the gas or the first electrolyte. The second supply unit supplies the second housing unit with the second electrolyte. The first carbon dioxide separation unit is connected to a discharge unit that discharges an emission containing oxygen and carbon dioxide from the second housing unit and separates the carbon dioxide from the gas component in the emission.

## SUMMARY

**[0011]** The conventional electrochemical $CO_2$ reduction device 200 that includes the carbon dioxide reactor described in JP 2021-147679 A requires the DAC process that recovers the dilute $CO_2$ in the atmosphere and concentrates it, in order to ensure the $CO_2$ gas at the high concentration as described above. Additionally, a process that desorbs the $CO_2$ recovered from the atmosphere as a $CO_2$ gas again is also required. Therefore, the conventional device took considerable energy for them, and the problem of high cost was not able to be solved.

**[0012]** In the problem, $CO_2$ recycling and/or circulation at low cost is expected by achieving an electrochemical $CO_2$ reduction device (a carbon dioxide recycling system) that does not require the process that recovers and/or concentrates $CO_2$ to obtain the $CO_2$ gas at the high concentration.

**[0013]** The present invention has been made in consideration of the situation. That is, an object of the present invention is to provide a carbon dioxide recycling system that eliminates a need for a process that recovers and/or concentrates $CO_2$ to obtain a $CO_2$ gas at a high concentration and allows generating a $CO_2$ reduction product.

**[0014]** A carbon dioxide recycling system in accordance with the present invention for solving the above problems, comprises: an electrochemical $CO_2$ reduction device that includes a reduction reaction electrode, an oxidation reaction electrode, and a first ion exchange membrane disposed between the reduction reaction electrode and the oxidation reaction electrode; and $CO_2$ gasification means that introduces a carbonate aqueous solution in which $CO_2$ is dissolved to a first half cell formed by including the reduction reaction electrode and the first ion exchange membrane as catholyte, and the $CO_2$ gasification means gasifying $CO_2$ in the catholyte immediately before reducing the $CO_2$ in the catholyte in the reduction reaction electrode.

**[0015]** According to the present invention, it is possible to provide a carbon dioxide recycling system that eliminates a need for a process that recovers and/or concentrates $CO_2$ to obtain a $CO_2$ gas at a high concentration and allows generating a $CO_2$ reduction product. Objects, configurations, and effects other than the above will be apparent from the description of the following embodiments.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0016]**

Fig. 1 is an overview diagram that describes an overall configuration of a carbon dioxide recycling system 1 according to one embodiment.

Fig. 2 is an overview diagram that describes an electrochemical $CO_2$ reduction device 10 in the carbon dioxide recycling system 1 according to one embodiment.

Fig. 3 is a graph (Bjerrum plot) showing a relationship between solubility of $CO_2$ to water and a pH.

Fig. 4 is an overview diagram that illustrates one example of an electrochemistry $CO_2$ gasifier 81 as one aspect of $CO_2$ gasification means 80.

Fig. 5 is an overview diagram illustrating an electrochemistry $CO_2$ gasifier 86 according to a first modification as one aspect of the $CO_2$ gasification means 80.

Fig. 6 is an overview diagram illustrating an electrochemistry $CO_2$ gasifier 89 according to a second modification as one aspect of the $CO_2$ gasification means 80.

Fig. 7 is an overview diagram illustrating an electrochemistry $CO_2$ gasifier 90 according to a third modification as another one aspect of the $CO_2$ gasification means 80.

Fig. 8 is an overview diagram illustrating an electrochemistry $CO_2$ gasifier 91 according to a fourth modification as another one aspect of the $CO_2$ gasification means 80.

Fig. 9 is an overview diagram illustrating an electrochemical $CO_2$ reduction device 14 according to the other aspect to describe another aspect of the $CO_2$ gasification means 80.

Fig. 10 is a configuration diagram illustrating one example of a $CO_2$ reuse mechanism 100.

Fig. 11 is a configuration diagram illustrating one example of a conventional electrochemical $CO_2$ reduction device 200.

## DETAILED DESCRIPTION

**[0017]** The following will describe a carbon dioxide recycling system 1 (hereinafter simply referred to as this system 1 in some cases) according to one embodiment of the present invention in detail with reference to the drawing appropriately.

**[0018]** In the description of each of embodiments, the identical reference numerals are given to a substantially identical or similar configuration, and when the description overlaps, the description is omitted in some cases.

### [Carbon Dioxide Recycling System 1]

**[0019]** Fig. 1 is an overview diagram that describes an overall configuration of the carbon dioxide recycling system 1 according to one embodiment.

**[0020]** As illustrated in Fig. 1, this system 1 includes an electrochemical $CO_2$ reduction device 10, a gas-liquid separation device (a cathode side) 20, a gas separation device (a cathode side) 30, a liquid extraction device (a cathode side) 40, a gas-liquid separation device (an anode side) 50, a gas separation device (an anode side) 60, and a liquid extraction device (an anode side) 70. A control device CD, such as a computer, controls all of operations by the devices. For example, to the electrochemical $CO_2$ reduction device 10, the gas separation device (the cathode side) 30, and the gas separation device (the anode side) 60, a power supply PS applies a voltage to electrodes (the cathode and the anode) disposed on them.

**[0021]** This system 1 supplies only an aqueous solution (a $CO_2$ dissolved aqueous solution) in which $CO_2$ is dissolved to the electrochemical $CO_2$ reduction device 10 (that is, does not supply a $CO_2$ gas at a high concentration), and generates a $CO_2$ reduction product. The $CO_2$ reduction product includes a carbon compound ($C_1$, $C_{2+}$) with carbon number 1 or 2 or more, that is, an organic compound, such as hydrocarbon. The electrochemical $CO_2$ reduction device 10 will be described later.

**[0022]** As the aqueous solution, for example, $CO_2$ recovery liquid (neutrality to alkalinity), a potassium carbonate aqueous solution, carbonated water, and seawater can be used. An example of the $CO_2$ recovery liquid includes water-soluble amine recovery liquid in which $CO_2$ is dissolved. In this embodiment, the above-described $CO_2$ dissolved aqueous solution, the $CO_2$ recovery liquid, and the like may be collectively referred to as a carbonate aqueous solution (a CAS).

**[0023]** Examples of $C_1$ and $C_{2+}$ include a gas, such as carbon monoxide (CO), methane ($CH_4$), ethane ($C_2H_6$), ethylene ($C_2H_4$), and formaldehyde ($CH_2O$), and liquid, such as methanol ($CH_3OH$), ethanol ($C_2H_5OH$), propanol ($C_3H_7OH$), formic acid ($CH_2O_2$), and acetaldehyde ($CH_3CHO$), but $C_1$ and $C_{2+}$ are not limited thereto.

**[0024]** In this system 1, $CO_2$ of the carbonate aqueous solution CAS supplied to the cathode side (a first half cell HC1) (see Fig. 2) of the electrochemical $CO_2$ reduction device 10 is electrolytically reduced by the device 10, and the $CO_2$ reduction product is generated as described above. A point that $CO_2$ in the carbonate aqueous solution CAS is electrolytically reduced in the first half cell HC1 will be described later.

**[0025]** Since the $CO_2$ reduction product generated in the electrochemical $CO_2$ reduction device 10 is a gas or liquid, gas-liquid separation is performed by the gas-liquid separation device (the cathode side) 20. The liquid separated by the gas-liquid separation device (the cathode side) 20 is transmitted to the liquid extraction device (the cathode side) 40, and, for example, extracted for each of chemical species, such as $C_2H_5OH$ and $C_3H_7OH$. This extraction can be performed by the known method using, for example, a difference in a boiling point.

**[0026]** Meanwhile, the gas separated by the gas-liquid separation device (the cathode side) 20 is transmitted to the gas separation device (the cathode side) 30, and, for example, separated for each of chemical species, such as $C_2H_6$, $CH_4$, carbon monoxide (CO), and hydrogen ($H_2$). This separation can be performed by the known method using, for example, adsorption and/or desorption actions to a gas separation membrane and an adsorbent.

**[0027]** $O_2$, the crossover $CO_2$, hydrogen peroxide ($H_2O_2$), and the like are generated on the anode side (the second half cell HC2) (see Fig. 2) of the electrochemical $CO_2$ reduction device 10. They are transmitted to the gas-liquid separation device (the anode side) 50 and gas-liquid separation is performed. The liquid (for example, $H_2O_2$) separated by the gas-liquid separation device (the anode side) 50 is transmitted to the liquid extraction device (the anode side) 70 and separated from water. This separation, for example, can be performed by distillation or the like but is not limited thereto.

**[0028]** Meanwhile, the gas separated by the gas-liquid separation device (the anode side) 50 is transmitted to the gas separation device (the anode side) 60 and separated into $O_2$ and crossover $CO_2$. This separation, for example, can be performed by the known method, such as a chemical absorption method, a physical absorption method, a solid absorption method, and membrane separation.

**[0029]** In the gas separation device (the cathode side) 30 and the gas separation device (the anode side) 60, an electrochemistry pH swing device using the known proton-coupled electron transfer (PCET) organic matter can be used or used in combination. The use of the electrochemistry pH swing device allows recovering only a $CO_2$ gas from a mixed gas component. When only the $CO_2$ gas can be recovered, it is considerably advantageous in reuse of the carbonate aqueous solution CAS.

**[0030]** That is, in this embodiment, the reuse mechanism 100 (see Fig. 10) that recovers at least one gas among a gas containing unreacted $CO_2$ discharged from the first half cell HC1 and a gas containing the crossover $CO_2$ discharged from the second half cell HC2, dissolves the gas in the carbonate aqueous solution CAS and causes the first half cell HC1 to reuse the carbonate aqueous solution CAS as the catholyte is preferably disposed. This allows reusing the unreacted $CO_2$ and the crossover $CO_2$, and therefore the usage efficiency of $CO_2$ is improved.

**[0031]** As the reuse mechanism 100, electrochemistry pH swing by the proton-coupled electron transfer (PCET) can be used. As described above, using dependence of ionization dissolution of $CO_2$ on a pH, the reuse mechanism 100 causes only $CO_2$ to actively transport from the cathode side to the anode side selectively by pH inclination to incrassate the $CO_2$. This allows selectively incrassating $CO_2$. Additionally, since $O_2$ or the like that is not ionized to be dissolved is not actively transported, a desorption process of desorbing only $CO_2$ can be eliminated.

[Electrochemical $CO_2$ Reduction Device]

**[0032]** Next, the electrochemical $CO_2$ reduction device 10 in this system 1 will be described in detail.

**[0033]** Fig. 2 is an overview diagram that describes the electrochemical $CO_2$ reduction device 10 in the carbon dioxide recycling system 1 according to one embodiment.

**[0034]** As illustrated in Fig. 2, the electrochemical $CO_2$ reduction device 10 includes a reduction reaction electrode 11 (a cathode), an oxidation reaction electrode 12 (anode), and a first ion exchange membrane 13 disposed between the reduction reaction electrode 11 and the oxidation reaction electrode 12.

**[0035]** In the electrochemical $CO_2$ reduction device 10 in this system 1, to the first half cell HC1 formed by including the reduction reaction electrode 11 and the first ion exchange membrane 13, the carbonate aqueous solution CAS in which $CO_2$ is dissolved is introduced as the catholyte.

**[0036]** In the electrochemical $CO_2$ reduction device 10, to the second half cell HC2 formed by including the oxidation reaction electrode 12 and the first ion exchange membrane 13, the carbonate aqueous solution CAS similar to the one described above is also introduced as anolyte.

**[0037]** The electrochemical $CO_2$ reduction device 10 includes $CO_2$ gasification means 80 (see Fig. 4 to Fig. 9) that gasifies $CO_2$ in the catholyte immediately before reducing $CO_2$ in the catholyte in the reduction reaction electrode 11. The $CO_2$ gasification means 80 will be described later.

**[0038]** For the reduction reaction electrode 11, for example, a cathode gas diffusion electrode (GDE) that includes a $CO_2$ reduction reaction catalyst (a cathode catalyst) in a gas diffusion layer (GDL) with a hydrophobic micro porous layer (MPL) is used. As the MPL, for example, one formed by water-repellent resin, such as polytetrafluoroethylene (PTFE) and fluorinated ethylene propylene (FEP), and carbon can be used. Examples of the cathode catalyst can include a metal material, such as copper (Cu), argentum (Ag), gold (Au), zinc (Zn), lead (Pb), indium (In), tin (Sn), cadmium (Cd), nickel (Ni), iron (Fe), platinum (Pt), and titanium (Ti), metal oxide thereof, and an alloy containing the metals. The cathode catalyst is not limited thereto, and as an organometal complex, such as ruthenium (Ru) and rhenium (Re), known as $CO_2$ reduction catalysts and a carbon material, such as graphene and carbon nanotube, may be used. The cathode catalyst can be disposed by application on a surface of the GDL with the MPL or the like. When $C_{2+}$ is the object as a $CO_2$ reduction product as the reduction reaction electrode 11, specifically, a CuO-NPs GDE that supports CuO nanoparticles on the surface of the GDL with the MPL by application can be used.

**[0039]** As the oxidation reaction electrode 12, for example, an anode GDE that includes an oxygen evolution reaction (OER) catalyst is used. As the anode GDE, for example, a metal material, such as platinum (Pt), gold (Au), nickel (Ni), cobalt (Co), palladium (Pd), iridium (Ir), manganese (Mn), iron (Fe), ruthenium (Ru), and titanium (Ti), metal oxide thereof, metal hydroxide, an alloy containing the metals, and a porous body formed of a metal complex thereof can be used. As the oxidation reaction electrode 12, a material known as an oxidation catalyst that can oxidize water ($H_2O$) and generate oxygen ($O_2$) and hydrogen peroxide ($H_2O_2$) can be widely used. Examples of the oxidation reaction electrode 12 may include a carbon material, such as carbon black, activated carbon, carbon nanotube, graphene, and diamond, transparent conductive oxide, such as indium tin oxide (ITO), zinc oxide (ZnO), and fluorine doped tin oxide (FTO), and further oxide semiconductor (such as $TiO_2$, $SrTiO_3$, $WO_3$, and $Fe_2O_3$), mixed anion semiconductor (such as oxysulfide $Y_2Ti_2O_5S_2$, acid halide $Bi_4NbO_8Cl$, and acid fluoride $Pb_2Ti_2O_{5.4}F_{1.2}$). As the oxidation reaction electrode 12, in order to increase an electrode reaction area to avoid reaction control of the OER, specifically, $IrO_2$ supported porous Ti felt, Ni foam, Pt mesh, and the like can be used.

**[0040]** The first ion exchange membrane 13 is, for example, preferably a bipolar membrane (BPM), but, for example, a cation-exchange membrane (CEM), an anion exchange membrane (AEM) can also be used. The BPM is an ion exchange membrane having a structure of stacking a CEM and an AEM. When a voltage (0.83 V) at a theoretical decomposition voltage of water or more is applied to both sides of the BPM, water in the membrane is decomposed to $H^+$ and OH , $H^+$ is supplied to the catholyte, and $OH^-$ is supplied to the anolyte.

**[0041]** Here, Table 1 and Table 2 show the cathode reaction and the anode reaction when the CEM is used as the first ion exchange membrane 13 ($H^+$ moves) and the cathode reaction and the anode reaction when the AEM is used ($OH^-$ moves), respectively. When the BPM is used as the first ion exchange membrane 13, even when there is a pH difference between the catholyte and the anolyte, the stably maintained pH of each electrolyte can be used.

Table 1

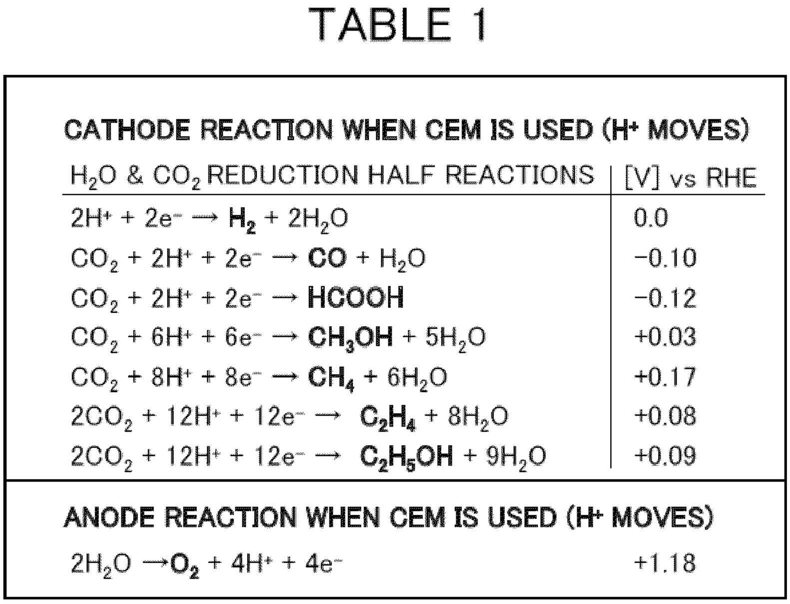


TABLE 1

**CATHODE REACTION WHEN CEM IS USED ($H^+$ MOVES)**

| $H_2O$ & $CO_2$ REDUCTION HALF REACTIONS | [V] vs RHE |
|---|---|
| $2H^+ + 2e^- \rightarrow \mathbf{H_2} + 2H_2O$ | 0.0 |
| $CO_2 + 2H^+ + 2e^- \rightarrow \mathbf{CO} + H_2O$ | −0.10 |
| $CO_2 + 2H^+ + 2e^- \rightarrow \mathbf{HCOOH}$ | −0.12 |
| $CO_2 + 6H^+ + 6e^- \rightarrow \mathbf{CH_3OH} + 5H_2O$ | +0.03 |
| $CO_2 + 8H^+ + 8e^- \rightarrow \mathbf{CH_4} + 6H_2O$ | +0.17 |
| $2CO_2 + 12H^+ + 12e^- \rightarrow \mathbf{C_2H_4} + 8H_2O$ | +0.08 |
| $2CO_2 + 12H^+ + 12e^- \rightarrow \mathbf{C_2H_5OH} + 9H_2O$ | +0.09 |

**ANODE REACTION WHEN CEM IS USED ($H^+$ MOVES)**

| | |
|---|---|
| $2H_2O \rightarrow \mathbf{O_2} + 4H^+ + 4e^-$ | +1.18 |

Table 2

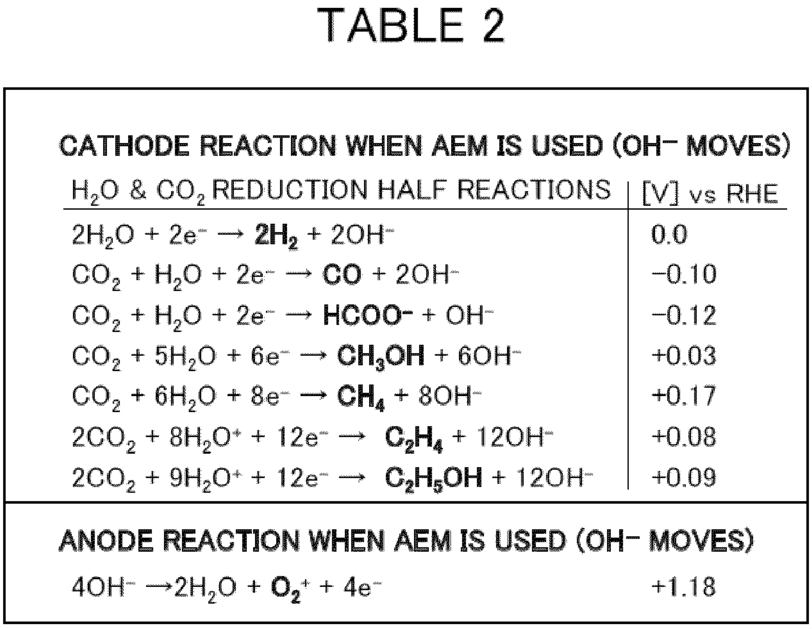


TABLE 2

**CATHODE REACTION WHEN AEM IS USED ($OH^-$ MOVES)**

| $H_2O$ & $CO_2$ REDUCTION HALF REACTIONS | [V] vs RHE |
|---|---|
| $2H_2O + 2e^- \rightarrow \mathbf{2H_2} + 2OH^-$ | 0.0 |
| $CO_2 + H_2O + 2e^- \rightarrow \mathbf{CO} + 2OH^-$ | −0.10 |
| $CO_2 + H_2O + 2e^- \rightarrow \mathbf{HCOO^-} + OH^-$ | −0.12 |
| $CO_2 + 5H_2O + 6e^- \rightarrow \mathbf{CH_3OH} + 6OH^-$ | +0.03 |
| $CO_2 + 6H_2O + 8e^- \rightarrow \mathbf{CH_4} + 8OH^-$ | +0.17 |
| $2CO_2 + 8H_2O^+ + 12e^- \rightarrow \mathbf{C_2H_4} + 12OH^-$ | +0.08 |
| $2CO_2 + 9H_2O^+ + 12e^- \rightarrow \mathbf{C_2H_5OH} + 12OH^-$ | +0.09 |

**ANODE REACTION WHEN AEM IS USED ($OH^-$ MOVES)**

| | |
|---|---|
| $4OH^- \rightarrow 2H_2O + \mathbf{O_2}^+ + 4e^-$ | +1.18 |

**[0042]** As described above, this system 1 does not receive the supply of the $CO_2$ gas at the high concentration but receives only the supply of the carbonate aqueous solution CAS to generate the $CO_2$ reduction product by the electrochemical $CO_2$ reduction device 10.

**[0043]** Here, in the electrochemistry $CO_2$ reduction, in a state where $CO_2$ is dissolved, namely, $HCO_3^-$ and $CO_3^{2-}$ , the $CO_2$ reduction reaction does not occur in the reduction reaction electrode 11.

**[0044]** However, as long as the dissolved $CO_2$ can be the $CO_2$ gas near the cathode catalyst of the reduction reaction electrode 11 inside the first half cell HC1 or immediately before the cathode catalyst, a three-phase interface reaction field of $CO_2$ (gas)-water (liquid)-catalyst (solid) can be formed, and therefore the $CO_2$ reduction reaction can be achieved.

**[0045]** As illustrated in Fig. 3, since solubility of $CO_2$ to water depends on a pH, this system 1 uses it. Fig. 3 is a graph (Bjerrum plot) showing a relationship between the solubility of $CO_2$ to water and the pH. In the drawing, the horizontal axis indicates the pH and the vertical axis indicates a dissolved inorganic carbon (DIC) rate.

**[0046]** As illustrated in Fig. 3, in the carbonic acid, the total concentration of the dissolved inorganic carbon changes by the change in pH of the aqueous solution (carbonate equilibrium). For example, pKa1 is present in the proximity of pH of 6, a $CO_2$ gas (g) increases on the alkaline side (pH of 6 or less), and vincreases on the neutral side (pH of 6 to 9). PKa2 is present in the proximity of pH of 9, and $CO_3^{2-}$ increases on the alkaline side (pH of 9 or more). In pKa1 and pKa2, the following equilibrated reactions are performed, respectively.

(pKa1) $H_2CO_3 + OH^- \Leftrightarrow HCO_3^- + H_2O$

(pKa2) $HCO_3^- + OH^- \Leftrightarrow CO_3^{2-} + H_2O$

Regarding $H_2O$, $H_2O \Leftrightarrow H^+ + OH^-$ is possibly generated.

**[0047]** As described above, when acidification occurs, $CO_2$ (g) flows out, and when alkalization occurs, $CO_2$ (g) is absorbed to increase the DIC.

$$DIC = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

**[0048]** As illustrated in Fig. 3, while $CO_2$ is present as ions (carbonate), such as $HCO_3^-$ and $CO_3^{2-}$ , in neutrality to alkalinity, $CO_2$ becomes a $CO_2$ gas in acidity. Therefore, using the property, this system 1 acidifies the carbonate aqueous solution CAS near the cathode catalyst or immediately before the cathode catalyst and supplies the carbonate dissolved in the carbonate aqueous solution CAS to the cathode catalyst as the $CO_2$ gas.

**[0049]** Thus, as one aspect of this system 1, by configuring the electrochemical $CO_2$ reduction device 10 including the $CO_2$ gasification means 80 that acidifies the carbonate aqueous solution CAS, the $CO_2$ reduction reaction can be achieved without ensuring or excessive supply of the $CO_2$ gas at the high concentration.

**[0050]** The $CO_2$ gasification means 80 can be formed by acidifying the carbonate aqueous solution CAS immediately before the introduction of the carbonate aqueous solution CAS in the first half cell HC1 or acidifying the carbonate aqueous solution CAS on the spot near the cathode catalyst. For example, the $CO_2$ gasification means 80 can be formed as follows.

## [One Aspect of $CO_2$ Gasification Means]

### (One Example of Electrochemistry $CO_2$ Gasifier)

**[0051]** Fig. 4 is an overview diagram that illustrates one example of an electrochemistry $CO_2$ gasifier 81 as one aspect of the $CO_2$ gasification means 80. Fig. 4 illustrates the electrochemical $CO_2$ reduction device 10 and the electrochemistry $CO_2$ gasifier 81.

**[0052]** As illustrated in Fig. 4, the electrochemistry $CO_2$ gasifier 81 according to one example includes a cathode 82 and an anode 83, a second ion exchange membrane 84 disposed between the cathode 82 and the anode 83, and a power supply 85 connected to the cathode 82 and the anode 83 and applies a voltage to them.

**[0053]** The electrochemistry $CO_2$ gasifier 81 includes a third half cell HC3 formed by including the cathode 82 and the second ion exchange membrane 84 and a fourth half cell HC4 formed by including the anode 83 and the second ion exchange membrane 84. The second ion exchange membrane 84 is, for example, preferably an AEM. To each of the third half cell HC3 and the fourth half cell HC4, the carbonate aqueous solution CAS (neutrality to alkalinity) is introduced.

**[0054]** The electrochemistry $CO_2$ gasifier 81 supplies $H^+$ in the carbonate aqueous solution CAS in the third half cell HC3 to which the voltage is applied by the cathode 82 and acidifies the carbonate aqueous solution CAS to gasify $CO_2$. The electrochemistry $CO_2$ gasifier 81 introduces the carbonate aqueous solution CAS containing the gasified $CO_2$ to the first half cell HC1 of the electrochemical $CO_2$ reduction device 10 as the catholyte.

**[0055]** Thus, the electrochemistry $CO_2$ gasifier 81 can stably and reliably introduce the carbonate aqueous solution CAS containing the gasified $CO_2$ to the first half cell HC1 of the electrochemical $CO_2$ reduction device 10.

**[0056]** In the electrochemistry $CO_2$ gasifier 81, to the carbonate aqueous solution CAS (neutrality to alkalinity) introduced to the third half cell HC3, $OH^-$ is supplied by the AEM and $OH^-$ is supplied by the anode 83, and therefore the pH becomes further high. The carbonate aqueous solution CAS with the further high pH is introduced to the second half cell HC2 of the electrochemical $CO_2$ reduction device 10.

### (First Modification of Electrochemistry $CO_2$ Gasifier)

**[0057]** Fig. 5 is an overview diagram illustrating an electrochemistry $CO_2$ gasifier 86 according to the first modification as one aspect of the $CO_2$ gasification means 80. Fig. 5 illustrates only the electrochemistry $CO_2$ gasifier 86.

**[0058]** As illustrated in Fig. 5, in the electrochemistry $CO_2$ gasifier 86 according to the first modification, the third half cell HC3 includes a first cation exchange membrane 87 between the cathode 82 and the second ion exchange membrane 84. Additionally, the electrochemistry $CO_2$ gasifier 86 includes a first redox medium RM1 between the cathode 82 and the first cation exchange membrane 87 and the carbonate aqueous solution CAS is introduced between the first cation exchange membrane 87 and the second ion exchange membrane 84.

**[0059]** Furthermore, in the electrochemistry $CO_2$ gasifier 86 according to the first modification, the fourth half cell HC4 includes a second cation exchange membrane 88 between the anode 83 and the second ion exchange membrane 84. The electrochemistry $CO_2$ gasifier 86 includes a second redox medium RM2 between the anode 83 and the second cation exchange membrane 88, and the carbonate aqueous solution CAS is introduced between the second cation exchange membrane 88 and the second ion exchange membrane 84.

**[0060]** The above-described first redox medium RM1 and second redox medium RM2 form a redox pair. Examples of the redox ions of the first redox medium RM1 and the second redox medium RM2 include $K_3[Fe(CN)_6]^{3-}/K_4[Fe(CN)_6]^{4-}$ and $IO_3^-/I^-$ , $Fe^{3+}/Fe^{2+}$, but the redox ions are not limited thereto. For example, as the redox ions, when $K_3[Fe(CN)_6]^{3-}/K_4[Fe(CN)_6]^{4-}$ is used, the following reactions occur in the cathode 82 and the anode 83, respectively.

Cathode:

$$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4}$$

Anode:

$$[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^-$$

**[0061]** The electrochemistry $CO_2$ gasifier 86 according to the first modification is disposed such that the first redox medium RM1 and the second redox medium RM2 circulate. Thus, concentration polarization of the redox ions by redox reaction of the electrode can be suppressed.

**[0062]** In the case of the electrochemistry $CO_2$ gasifier 86 according to the first modification, the second ion exchange membrane 84 uses the BPM. Both of the first cation exchange membrane 87 of the third half cell HC3 and the second cation exchange membrane 88 of the fourth half cell HC4 only need to be the CEM. The first cation exchange membrane 87 and the second cation exchange membrane 88 are preferably the same kind but may be different kinds. Although the CEM does not transmit the redox ions but transmits counter ions.

**[0063]** In the electrochemistry $CO_2$ gasifier 86 having the configuration illustrated in Fig. 5, the $CO_2$ gas is generated in the catholyte that is acidified by the supply of $H^+$ in the third half cell HC3, and it remains in bicarbonate ions or carbonate ions in the anolyte that is alkalized by the supply of $OH^-$ in the fourth half cell HC4. The catholyte is supplied to the first half cell HC1 of the electrochemical $CO_2$ reduction device 10, and the anolyte is supplied to the second half cell HC2 of the electrochemical $CO_2$ reduction device 10.

**[0064]** The electrochemistry $CO_2$ gasifier 86 applies a voltage to the cathode 82 and the anode 83 via conducting wires, and performs both generation of $H^+$ and $OH^-$ in the BPM (the second ion exchange membrane 84) and the redox reaction of redox ions in the anode 83 and the cathode 82 to ensure continuous catholyte acidification on the carbonate aqueous solution CAS and $CO_2$ gasification.

### (Second Modification of Electrochemistry $CO_2$ Gasifier)

**[0065]** Fig. 6 is an overview diagram illustrating an electrochemistry $CO_2$ gasifier 89 according to the second modification as one aspect of the $CO_2$ gasification means 80. Fig. 6 illustrates only the electrochemistry $CO_2$ gasifier 89 according to the second modification.

**[0066]** As illustrated in Fig. 6, the electrochemistry $CO_2$ gasifier 89 according to the second modification differs from the electrochemistry $CO_2$ gasifier 86 according to the first modification illustrated in Fig. 5 in that a temperature difference is given between the cathode 82 and the anode 83, but the others are similar.

**[0067]** Therefore, here, the aspect of giving the temperature difference between the cathode 82 and the anode 83, which is the difference, will be described.

**[0068]** In the aspect, from a principle of a thermochemical battery (temperature difference power generation), by giving the temperature difference between the cathode 82 and the anode 83, power can be generated by thermoelectromotive force (the following formula 1), and an operation without an external power supply is possible. For example, in an N type redox, an oxidant (Ox) becomes a reductant (Red) on a high temperature side $T_{hot}$, and Red becomes Ox on a low temperature side $T_{cold}$ (the following formula 2).

Math. 1

$$\text{THERMOELECTROMOTIVE FORCE: } \alpha = \frac{\partial V}{\partial T} = \frac{\Delta S_{ox,Red}}{nF} \quad \cdots\text{(FORMULA 1)}$$

Ox: OXIDANT
Red: REDUCTANT
S: ENTROPY
F: FARADAY CONSTANT

Math. 2

$$Ox + e^- \underset{T_{COLD}}{\overset{T_{HOT}}{\rightleftarrows}} Red \qquad \cdots\text{(FORMULA 2)}$$

**[0069]** The electrochemistry $CO_2$ gasifier 89 according to the second modification illustrated in Fig. 6 includes a heat source (a high temperature side) 82h in the cathode 82 and a heat source (a low temperature side) 83c in the anode 83. The temperature difference only needs to occur between the cathode 82 and the anode 83, and only any one of the heat sources may be disposed. Additionally, as described above, the heat sources can be without the external power supply, but can be heated and cooled using the external power supply. Without the external power supply, heat and cold generated in an external device can be used.

(Third Modification of Electrochemistry $CO_2$ Gasifier)

**[0070]** Fig. 7 is an overview diagram illustrating an electrochemistry $CO_2$ gasifier 90 according to the third modification as another one aspect of the $CO_2$ gasification means 80. Fig. 7 illustrates the electrochemical $CO_2$ reduction device 10 and the electrochemistry $CO_2$ gasifier 90 according to the third modification.

**[0071]** As illustrated in Fig. 7, in the electrochemistry $CO_2$ gasifier 90 according to the third modification, the third half cell HC3 of the device 90 is connected to the first half cell HC1 and the second half cell HC2 of the electrochemical $CO_2$ reduction device 10.

**[0072]** The electrochemistry $CO_2$ gasifier 90 according to the third modification introduces the carbonate aqueous solution CAS containing $CO_2$ gasified in the third half cell HC3 to the first half cell HC1 as the catholyte and introduces the carbonate aqueous solution CAS to the second half cell HC2 formed by including the oxidation reaction electrode 12 and the first ion exchange membrane 13 as the anolyte.

**[0073]** The catholyte introduced to the first half cell HC1 of the electrochemical $CO_2$ reduction device 10 is acidified in the third half cell HC3 of the electrochemistry $CO_2$ gasifier 90 according to the third modification, and $CO_2$ is gasified. Therefore, as described above, the $CO_2$ reduction product ($C_1$, $C_{2+}$) can be generated by the reduction reaction electrode 11.

**[0074]** While the anolyte introduced to the second half cell HC2 of the electrochemical $CO_2$ reduction device 10 is acidified in the third half cell HC3 of the electrochemistry $CO_2$ gasifier 90 according to the third modification, since $OH^-$ is supplied in the second half cell HC2, the anolyte becomes neutrality to alkalinity. Therefore, the gasified $CO_2$ again becomes the carbonate ($HCO_3^-$, $CO_3^{2-}$) and the carbonate is dissolved in the carbonate aqueous solution CAS. Since the carbonate aqueous solution CAS becomes neutrality to alkalinity, by contact with the $CO_2$ gas that is unreacted in the first half cell HC1 of the electrochemical $CO_2$ reduction device 10 separately, the unreacted $CO_2$ gas can be redissolved in the carbonate aqueous solution CAS. In this embodiment, the carbonate aqueous solution CAS in which the $CO_2$ gas unreacted in the first half cell HC1 of the electrochemical $CO_2$ reduction device 10 is redissolved is referred to as recovered electrolyte in some cases. That is, in this embodiment, since the recovered electrolyte is reused, as the carbonate aqueous solution CAS, the $CO_2$ reduction product can be generated. Thus, the usage efficiency of $CO_2$ is improved.

**[0075]** The recovered electrolyte further can perform supply to the third half cell HC3 again after supply to the fourth half cell HC4 of the electrochemistry $CO_2$ gasifier 90. Since $OH^-$ is supplied to the recovered electrolyte in the fourth half cell HC4, the pH can be high. Accordingly, the $CO_2$ gas can be dissolved with more certainty.

(Fourth Modification of Electrochemistry $CO_2$ Gasifier)

**[0076]** Fig. 8 is an overview diagram illustrating an electrochemistry $CO_2$ gasifier 91 according to the fourth modification as another one aspect of the $CO_2$ gasification means 80. Fig. 8 illustrates only the electrochemistry $CO_2$ gasifier 91 according to the fourth modification.

**[0077]** As illustrated in Fig. 8, in the electrochemistry $CO_2$ gasifier 91 according to the fourth modification, the cathode 82 and the anode 83 are configured as PCET electrodes that perform the proton-coupled electron transfer (PCET) reaction. In the cathode 82 and the anode 83 in the electrochemistry $CO_2$ gasifier 91, the following reaction progresses. In the following formula, X(s) indicates the PCET electrode.

$$X(s) + nH^+ + ne^- \Leftrightarrow XHn(s)$$

**[0078]** That is, in the electrochemistry $CO_2$ gasifier 91, by the electrochemical reaction, the proton $H^+$ can be reversibly inserted to and desorbed from the PCET electrode.

**[0079]** As the PCET electrode, for example, metal oxide, such as $MnO_2$, $CoO_2$, and $NiO_2$, can be used, but the PCET electrode is not limited thereto.

**[0080]** The method of using the PCET electrode can apply an aqueous solution different from the method of using PCET organic molecules that can be applied to only an aprotic solvent (organic solvent, ionic liquid).

**[0081]** In the modification, the second ion exchange membrane 84 is an AEM. The known AEM can be used.

**[0082]** In the electrochemistry $CO_2$ gasifier 91 according to the fourth modification of the configuration, from the PCET electrode that serves as the anode 83 that is a + pole by application of a positive electric potential, $H^+$ is supplied to the aqueous solution and the pH lowers, and to the PCET electrode that serves as the cathode 82 that is a - pole, $H^+$ is supplied from the aqueous solution to the PCET electrode, and the pH becomes high. When the pH lowers, $H^+$ reacts to $HCO_3^-$, and the $CO_2$ gas is generated. The acidified aqueous solution is introduced to the first half cell HC1 of the electrochemical $CO_2$ reduction device 10 as the catholyte in which $CO_2$ is gasified.

**[0083]** On the other hand, the recovered electrolyte at the low pH is introduced to the fourth half cell HC4 of the electrochemistry $CO_2$ gasifier 91 according to the fourth modification. Since in the recovered electrolyte at the low pH, $OH^-$ passes through the AEM to be supplied, and therefore the low pH becomes high. Therefore, the recovered electrolyte can be regenerated as the carbonate aqueous solution CAS obtained by dissolving $CO_2$ in a state of bicarbonate ions ($HCO_3^-$) and carbonate ions ($CO_3^{2-}$).

**[0084]** In the electrochemistry $CO_2$ gasifier 91 according to the fourth modification, periodic electric potential switching (polarity reversion) of the PCET electrode is synchronized with switching of a supply passage of the carbonate aqueous solution CAS (namely, the catholyte) to at least the first half cell HC1. Thus, in this embodiment, the continuous $CO_2$ reduction reaction can be performed.

[Another Aspects of $CO_2$ Gasification Means]

**[0085]** Fig. 9 is an overview diagram illustrating an electrochemical $CO_2$ reduction device 14 according to the other aspect to describe another aspect of the $CO_2$ gasification means 80.

**[0086]** As illustrated in Fig. 9, in $CO_2$ gasification means 80Ain the electrochemical $CO_2$ reduction device 14 according to another aspect, the first ion exchange membrane 13 is preferably a BPM. With $H^+$ supplied from the BPM, the catholyte is locally acidified at the proximity (on the spot) of the reduction reaction electrode 11, and this gasifies $CO_2$ in the catholyte.

**[0087]** The reduction reaction electrode 11 is a GDE with a $CO_2$ reduction reaction catalyst, and the oxidation reaction electrode 12 is a GDE with an OER catalyst.

**[0088]** As examples of a chemical reaction in the electrochemical $CO_2$ reduction device 14 having such a configuration, a reaction $\alpha$, a reaction $\beta$, a reaction $\gamma$, and a reaction $\delta$ illustrated in Fig. 9 occur.

(Reaction $\alpha$) $4OH^- \rightarrow O_2 + 2H_2O + e^-$

(Reaction $\beta$) $4H_2O \rightarrow 4H^+ + 4OH^-$

(Reaction $\gamma$) $2CO_3^{2-} + 4H^+ \rightarrow 2CO_2(g) + 2H_2O$

(Reaction δ) $CO_2(g) + e^- + H_2O \rightarrow C_xH_yO_z + OH^-$

**[0089]** In the other aspect, the catholyte is supplied as the neutral to alkaline carbonate aqueous solution CAS together with anolyte. However, as described above, since the catholyte is locally acidified by $H^+$ supplied from the BPM in the cathode chamber (the first half cell HC1), $CO_2$ can be reacted to the cathode catalyst as the $CO_2$ gas. That is, in the aspect, although the carbonate aqueous solution CAS in the state of the carbonate being dissolved in the first half cell HC1 is suppled, the $CO_2$ gas can be generated near the cathode three-phase interface reaction field, it can be reduced, and the $CO_2$ reduction product can be generated.

(Example of $CO_2$ Reuse Mechanism)

**[0090]** One aspect of the reuse mechanism has been described above. Here, another specific aspect of the above-described reuse mechanism will be described. Fig. 10 is a configuration diagram illustrating one example of a $CO_2$ reuse mechanism 100.

**[0091]** As illustrated in Fig. 10, the $CO_2$ reuse mechanism 100 includes a cathode GDE 101, an anode GDE 102, and a quinone solution layer 103 containing a quinone compound as a PCET organic matter and the like between the cathode GDE 101 and the anode GDE 102. That is, the reuse mechanism 100 illustrated in Fig. 10 is an electrochemistry pH swing device using the PCET organic matter.

**[0092]** The gas introduced to the $CO_2$ reuse mechanism 100 is one after the gas-liquid separation of the $CO_2$ reduction product from the electrochemical $CO_2$ reduction device 10 and one after the gas-liquid separation of the crossover $CO_2$, and therefore liquid is absent. The gas is a mixed gas containing $CO_2$ at a comparatively thin concentration in which the unreacted $CO_2$, the gas generated in the reaction (such as $O_2$), the crossover $CO_2$, or the like is mixed.

**[0093]** The reuse mechanism 100 introduces the gas from the cathode GDE 101 to the quinone solution layer 103 to perform the PCET reaction, and thus the $CO_2$ concentration is increased to recover $CO_2$ from the anode GDE 102. While the $CO_2$ among the gas introduced from the cathode GDE 101 side is dissolved in the quinone solution layer 103, a gas other than that (for example, $N_2$ and $O_2$) is not dissolved. Mostly, $CO_2$ is selectively dissolved and afterwards concentrated. The $CO_2$ recovered from the anode GDE 102 is actively transported selectively by pH inclination and therefore has the high concentration. $CO_2$ is preferably recovered by sweeping with a gas. Examples of the gas to sweep include an inert gas, such as Ar, and $H_2O$. The above-described quinone solution layer 103 is preferably a solution obtained by dissolving the quinone compound in an aprotic solvent (an organic solvent and ionic liquid), but is not limited thereto. For example, the quinone solution layer 103 may be a separator holding a quinone solution containing 1M or less of a $NaHCO_3$ aqueous solution.

**[0094]** In the cathode GDE 101 and the anode GDE 102 of the reuse mechanism 100, the following reaction progresses. By the reaction, the pH increases on the cathode GDE 101 side and the pH lowers on the anode GDE 102 side of the reuse mechanism 100. In the following formula, Q indicates quinone. Q serves as an oxidant (Ox) and $QH_2$ serves as a reductant (Red).

(Cathode) $Q + 2e^- + 2H^+ \rightarrow QH_2$

(Anode) $QH_2 \rightarrow Q + 2e^- + 2H^+$

$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$

All reactions of the anode GDE 102 is as follows. (All reactions of the anode)

$2HCO_3^- + QH_2 \rightarrow Q + 2CO_2 + 2H_2O$

[Other Preferred Aspects]

**[0095]** In the carbon dioxide recycling system 1 according to the embodiment, the catholyte preferably contains at least one of $K^+$ and $Na^+$. Thus, adsorption of $K^+$ and $Na^+$ on the surface of the cathode catalyst of the reduction reaction electrode 11 allows suppressing the adsorption of $H^+$. Therefore, hydrogen electrode reaction (HER) advantageous in the acidic environment can be suppressed.

**[0096]** In the preferred aspect, $K^+$ and $Na^+$ are preferably one obtained by addition to the catholyte as KCl or NaCl at a concentration of 0.5 to 3 M. Thus, the HER advantageous in the acidic environment can be suppressed with more certainty.

**[0097]** In the above-described embodiment, as the reduction reaction electrode 11 of the electrochemical $CO_2$ reduction device 10, for example, the use of the cathode GDE including the $CO_2$ reduction reaction catalyst in the GDL with the MPL has been described, but this embodiment is not limited thereto. In the above-described embodiment, for example, the use of the anode GDE that includes the OER catalyst as the oxidation reaction electrode 12 of the electrochemical $CO_2$ reduction device 10 has been described, but this embodiment is not limited thereto.

**[0098]** In this embodiment, the electrode structures of the reduction reaction electrode 11 and the oxidation reaction electrode 12 only need to be a thin film shape, a grid shape, a particle shape, a wire shape, or a porous shape, and can be used not limited to the one described above. Both of the reduction reaction electrode 11 and the oxidation reaction electrode 12 formed by the electrode structures can perform the $CO_2$ gas reduction reaction and the oxygen evolution reaction from $H_2O$ described above.

**[0099]** While the carbon dioxide recycling system 1 according to the present invention has been described in detail by the embodiments, the present invention is not limited to the above-described embodiments but various modifications are included. For example, the embodiments described above have been described in detail to simply describe the present invention, and are not necessarily required to include all the described configurations. In addition, part of the configuration of one embodiment can be replaced with the configurations of other embodiments, and in addition, the configuration of the one embodiment can also be added with the configurations of other embodiments. In addition, part of the configuration of each of the embodiments can be subjected to addition, deletion, and replacement with respect to other configurations.

## Claims

1. A carbon dioxide recycling system, comprising:

    an electrochemical $CO_2$ reduction device that includes a reduction reaction electrode, an oxidation reaction electrode, and a first ion exchange membrane disposed between the reduction reaction electrode and the oxidation reaction electrode; and
    $CO_2$ gasification means that introduces a carbonate aqueous solution in which $CO_2$ is dissolved to a first half cell formed by including the reduction reaction electrode and the first ion exchange membrane as catholyte, and the $CO_2$ gasification means gasifying $CO_2$ in the catholyte immediately before reducing the $CO_2$ in the catholyte in the reduction reaction electrode.

2. The carbon dioxide recycling system according to claim 1, wherein

    the $CO_2$ gasification means is an electrochemistry $CO_2$ gasifier,
    the electrochemistry $CO_2$ gasifier includes:

        a cathode and an anode;
        a second ion exchange membrane disposed between the cathode and the anode; and
        a power supply connected to the cathode and the anode and applying a voltage to the cathode and the anode,

    the carbonate aqueous solution is introduced to each of a third half cell formed by including the cathode and the second ion exchange membrane and a fourth half cell formed by including the anode and the second ion exchange membrane, and
    in the third half cell to which the voltage is applied, the $CO_2$ in the carbonate aqueous solution is gasified by the cathode, and the carbonate aqueous solution containing the gasified $CO_2$ is introduced to the first half cell as the catholyte.

3. The carbon dioxide recycling system according to claim 2, wherein

    the third half cell includes a first cation exchange membrane between the cathode and the second ion exchange membrane and includes a first redox medium between the cathode and the first cation exchange membrane, and the carbonate aqueous solution is introduced between the first cation exchange membrane and the second ion exchange membrane,
    the fourth half cell includes a second cation exchange membrane between the anode and the second ion exchange membrane and includes a second redox medium between the anode and the second cation exchange membrane, and the carbonate aqueous solution is introduced between the second cation exchange membrane and the second ion exchange membrane, and
    the first redox medium and the second redox medium are disposed to circulate.

**4.** The carbon dioxide recycling system according to claim 3, wherein
a temperature difference is given between the cathode and the anode.

**5.** The carbon dioxide recycling system according to claim 2, wherein

the carbonate aqueous solution containing the gasified $CO_2$ is introduced to the first half cell as the catholyte and is introduced to a second half cell formed by including the oxidation reaction electrode and the first ion exchange membrane as anolyte, and
a carbonate aqueous solution introduced to the fourth half cell includes a carbonate aqueous solution containing unreacted $CO_2$ recovered from the first half cell.

**6.** The carbon dioxide recycling system according to claim 2, wherein

both of the cathode and the anode are PCET electrodes that perform a proton-coupled electron transfer reaction,
the second ion exchange membrane is an anion exchange membrane, and
periodic electric potential switching to the PCET electrode is synchronized with at least switching of a supply passage of the carbonate aqueous solution to the first half cell.

**7.** The carbon dioxide recycling system according to claim 1, wherein

in the $CO_2$ gasification means,
the first ion exchange membrane is a bipolar membrane, and
the catholyte is locally acidified at a proximity of the reduction reaction electrode with $H^+$ supplied from the bipolar membrane to gasify the $CO_2$ in the catholyte.

**8.** The carbon dioxide recycling system according to claim 1, comprising:

a second half cell formed by including the oxidation reaction electrode and the first ion exchange membrane; and
a reuse mechanism that recovers at least one of a gas containing unreacted $CO_2$ discharged from the first half cell and a gas containing crossover $CO_2$ discharged from the second half cell, dissolves the gas in the carbonate aqueous solution, and causes the first half cell to reuse the carbonate aqueous solution as catholyte.

**9.** The carbon dioxide recycling system according to claim 8, wherein
using dependance of ionization dissolution of the $CO_2$ on a pH, the reuse mechanism actively transports only $CO_2$ from a cathode side to an anode side selectively by pH inclination to incrassate the $CO_2$.

**10.** The carbon dioxide recycling system according to claim 8, wherein

in the reuse mechanism, a quinone solution layer is disposed between the cathode and the anode, and
the gas is introduced from the cathode to the quinone solution, and a proton-coupled electron transfer reaction is performed to increase a $CO_2$ concentration and recover the $CO_2$ from the anode.

**11.** The carbon dioxide recycling system according to claim 1, wherein
the catholyte contains at least one of $K^+$ and $Na^+$.

**12.** The carbon dioxide recycling system according to claim 11, wherein
the $K^+$ or the $Na^+$ are added to the catholyte as KCl or NaCl at a concentration of 0.5 to 3 M.

**13.** The carbon dioxide recycling system according to claim 1, wherein
the first ion exchange membrane is a cation exchange membrane or an anion exchange membrane.

**14.** The carbon dioxide recycling system according to claim 1, wherein
the reduction reaction electrode and the oxidation reaction electrode have an electrode structure of a thin film shape, a grid shape, a particle shape, a wire shape, or a porous shape.

**15.** The carbon dioxide recycling system according to claim 1, wherein
the carbonate aqueous solution is water-soluble amine recovery liquid, a potassium carbonate aqueous solution, carbonated water, or seawater, in which $CO_2$ is dissolved.

FIG. 1

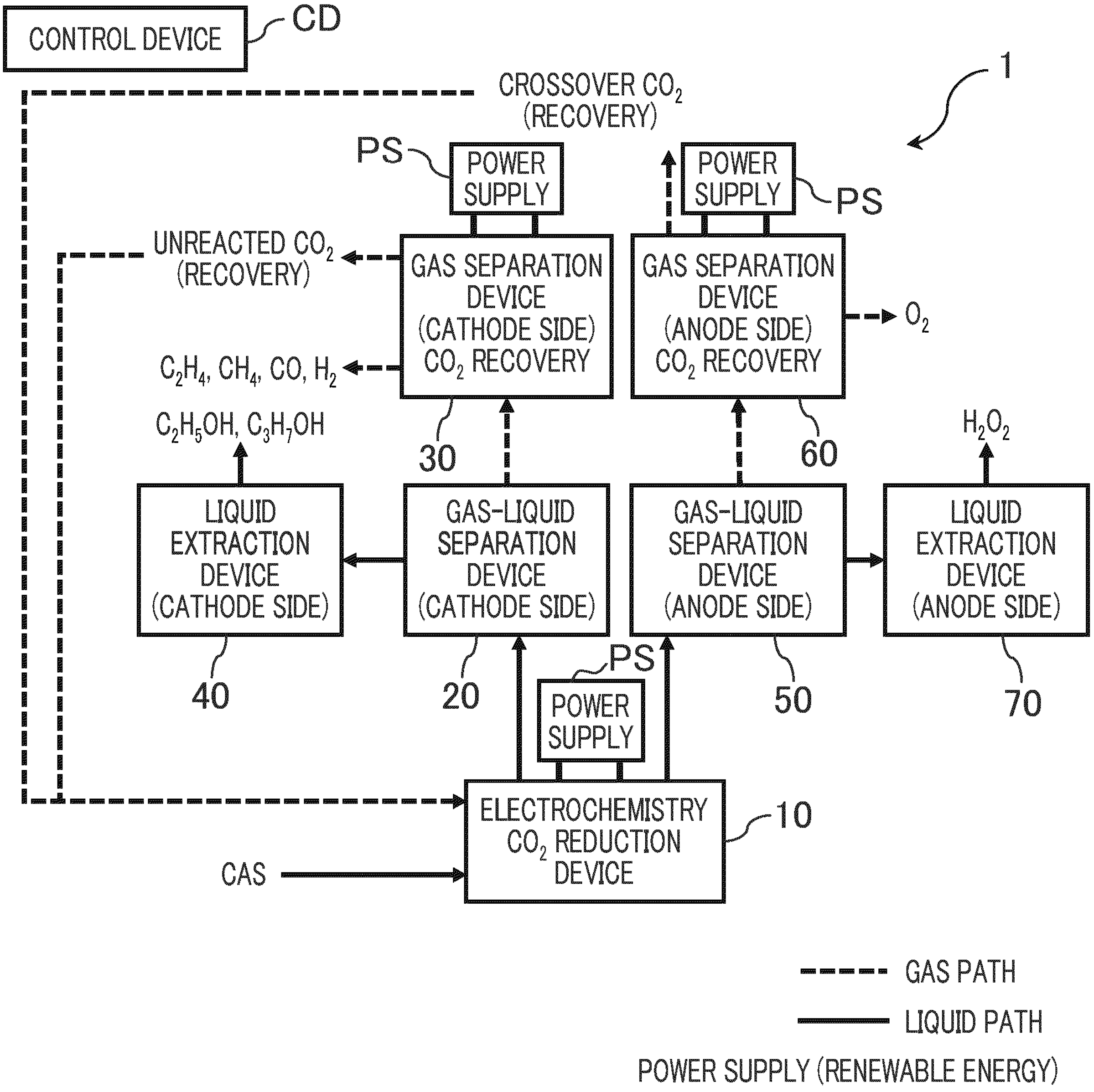

CONTROL DEVICE
CD
1
CROSSOVER $CO_2$ (RECOVERY)
PS
POWER SUPPLY
POWER SUPPLY
PS
UNREACTED $CO_2$ (RECOVERY)
GAS SEPARATION DEVICE (CATHODE SIDE) $CO_2$ RECOVERY
GAS SEPARATION DEVICE (ANODE SIDE) $CO_2$ RECOVERY
$O_2$
$C_2H_4$, $CH_4$, CO, $H_2$
$C_2H_5OH$, $C_3H_7OH$
30
60
$H_2O_2$
LIQUID EXTRACTION DEVICE (CATHODE SIDE)
GAS-LIQUID SEPARATION DEVICE (CATHODE SIDE)
GAS-LIQUID SEPARATION DEVICE (ANODE SIDE)
LIQUID EXTRACTION DEVICE (ANODE SIDE)
PS
40
20
50
70
POWER SUPPLY
ELECTROCHEMISTRY $CO_2$ REDUCTION DEVICE
10
CAS
GAS PATH
LIQUID PATH
POWER SUPPLY (RENEWABLE ENERGY)

FIG. 2

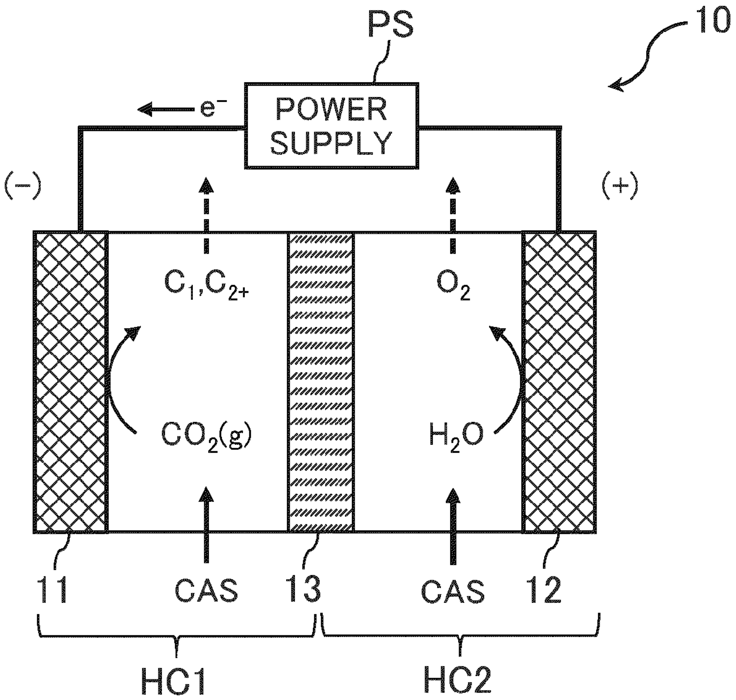

PS
10
POWER SUPPLY
$e^-$
(−)
(+)
$C_1,C_{2+}$
$O_2$
$CO_2(g)$
$H_2O$
11
CAS
13
CAS
12
HC1
HC2

FIG. 3

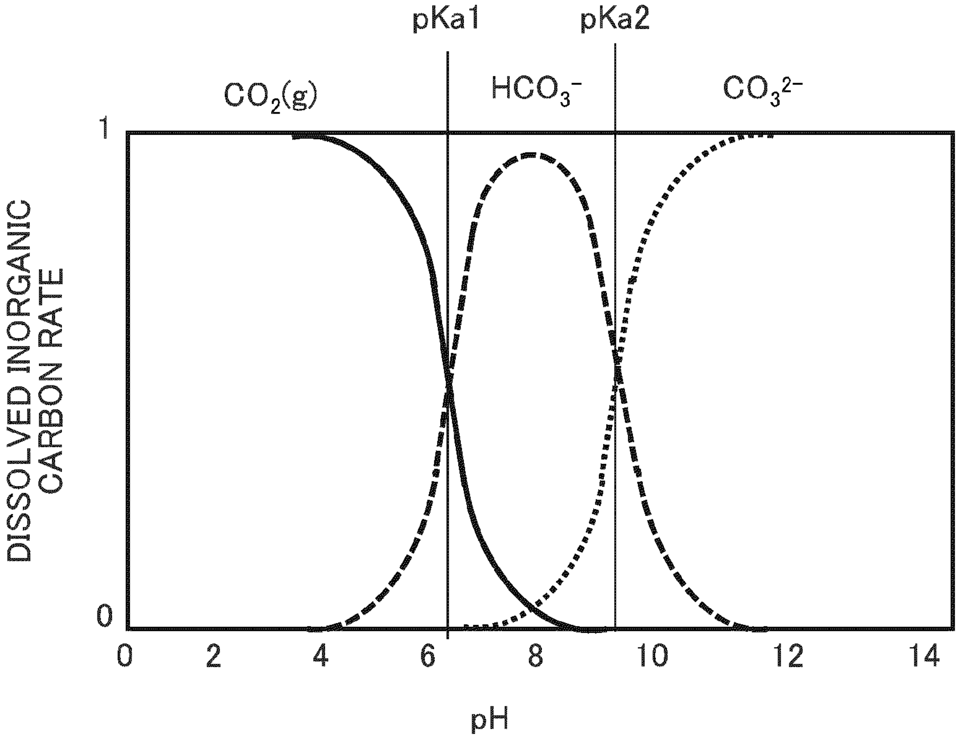

pKa1
pKa2
$CO_2(g)$
$HCO_3^-$
$CO_3^{2-}$
1
0
DISSOLVED INORGANIC CARBON RATE
0
2
4
6
8
10
12
14
pH

FIG. 4

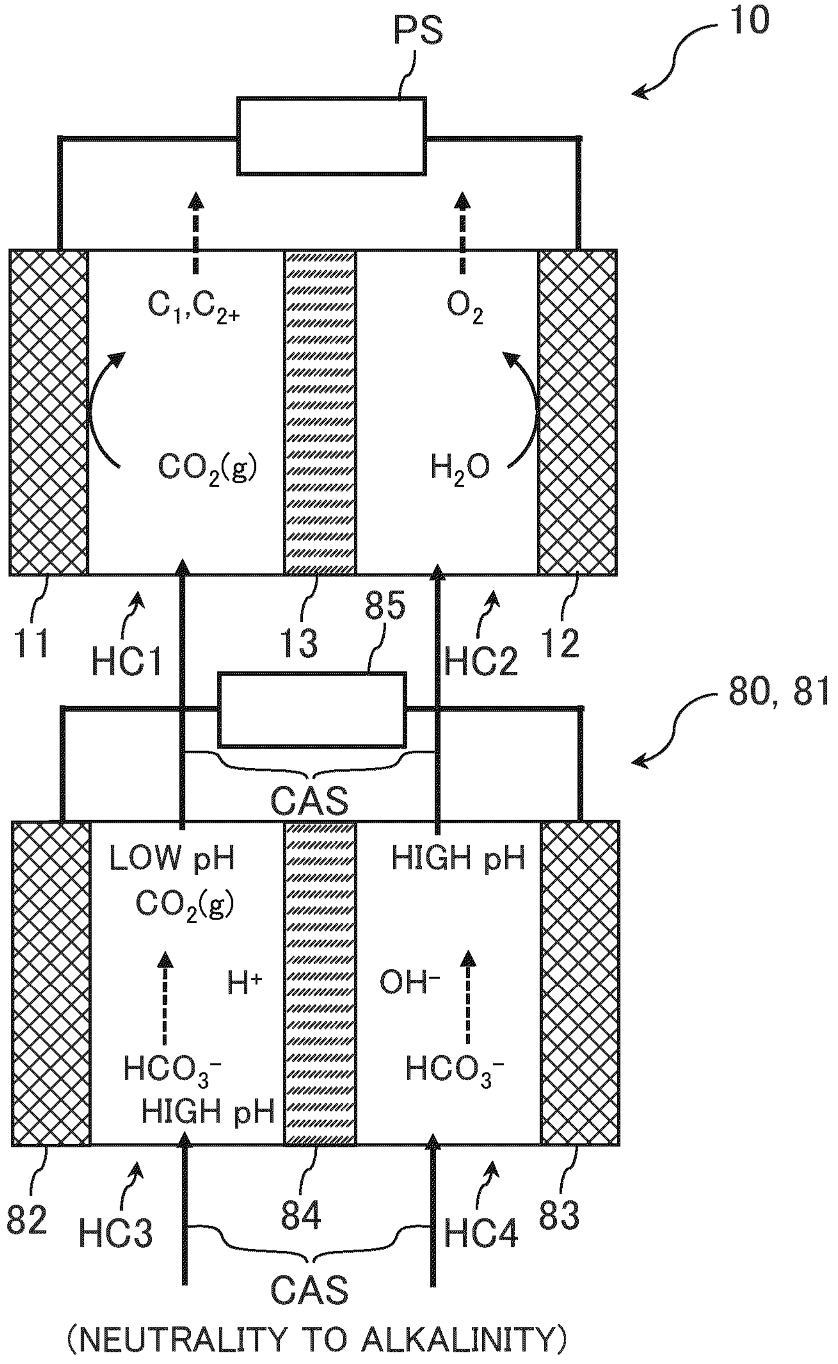

PS
10
$C_1$,$C_{2+}$
$O_2$
$CO_2$(g)
$H_2O$
11
HC1
13
85
HC2
12
80, 81
CAS
LOW pH
$CO_2$(g)
HIGH pH
$H^+$
$OH^-$
$HCO_3^-$
HIGH pH
$HCO_3^-$
82
HC3
84
HC4
83
CAS
(NEUTRALITY TO ALKALINITY)

FIG. 5

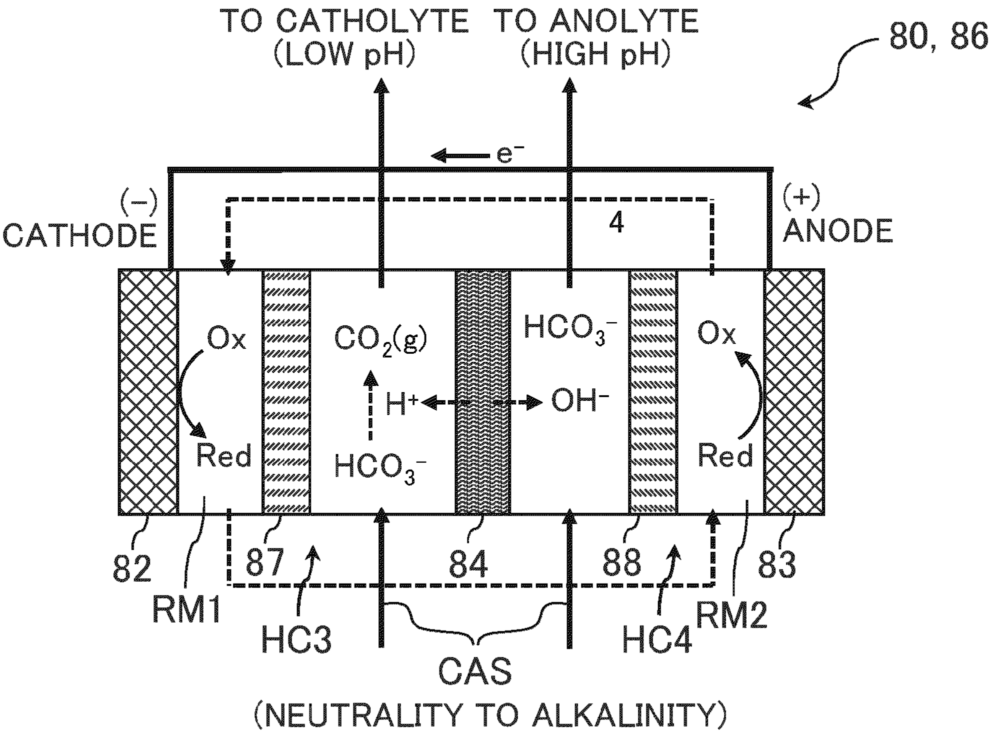

TO CATHOLYTE
(LOW pH)
TO ANOLYTE
(HIGH pH)
80, 86
e⁻
(−)
CATHODE
(+)
ANODE
4
Ox
Red
CO2(g)
H⁺
HCO3⁻
HCO3⁻
OH⁻
Ox
Red
82
RM1
87
HC3
84
CAS
(NEUTRALITY TO ALKALINITY)
88
HC4
RM2
83

FIG. 6

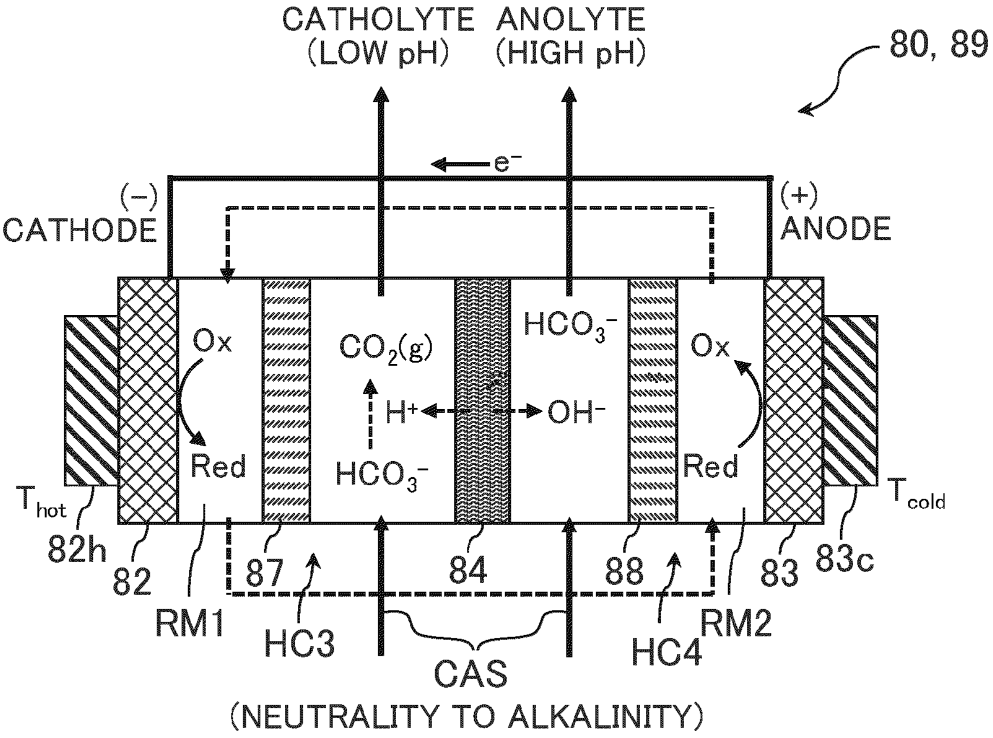

CATHOLYTE
(LOW pH)
ANOLYTE
(HIGH pH)
80, 89
e⁻
(−)
CATHODE
(+)
ANODE
Ox
Red
CO2(g)
H⁺
HCO3⁻
HCO3⁻
OH⁻
Ox
Red
Thot
82h
82
RM1
87
HC3
84
CAS
(NEUTRALITY TO ALKALINITY)
88
HC4
RM2
83
83c
Tcold

FIG. 7

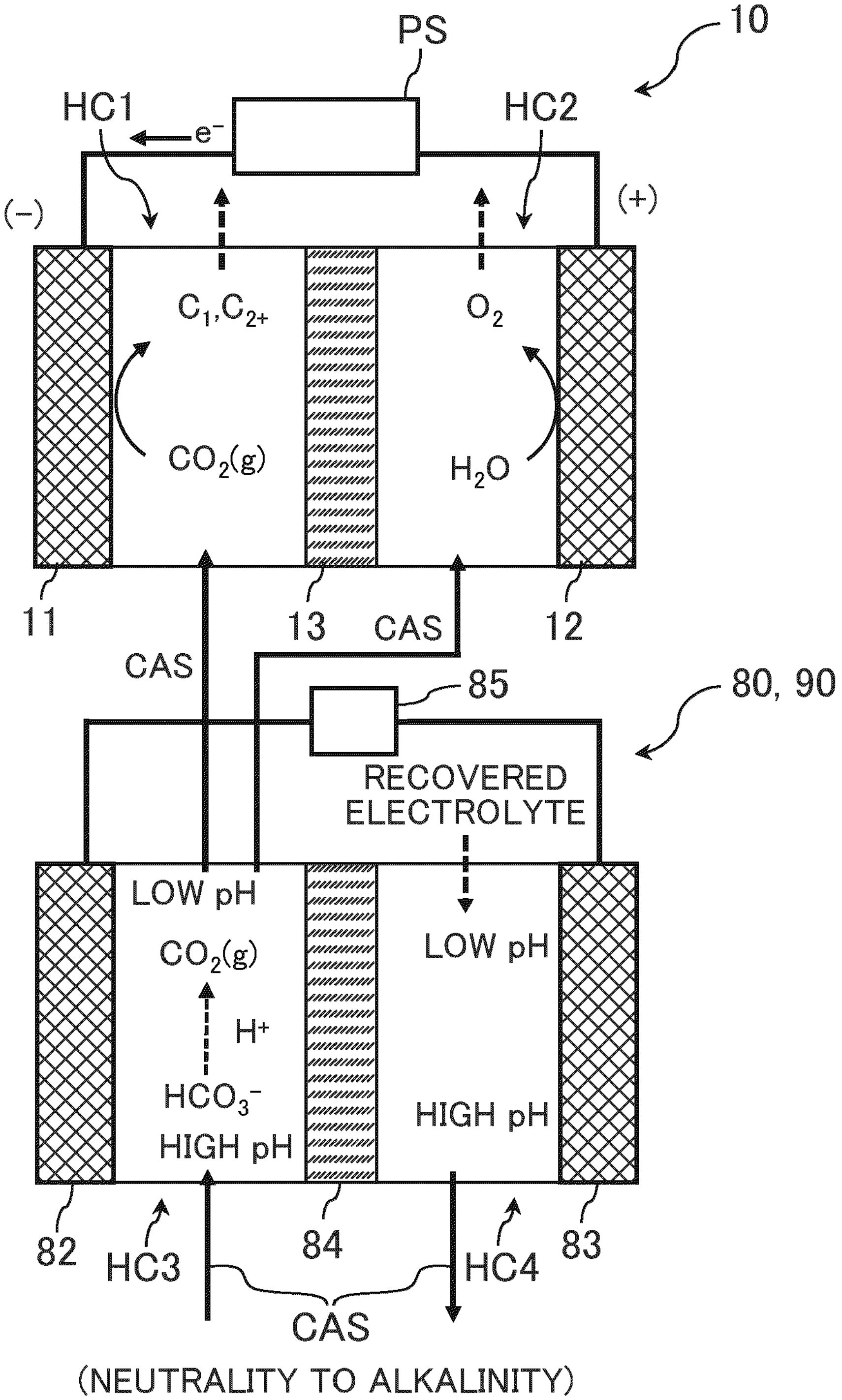

10
PS
HC1
$e^-$
HC2
(−)
(+)
$C_1,C_{2+}$
$O_2$
$CO_2(g)$
$H_2O$
11
13
CAS
12
CAS
85
80, 90
RECOVERED ELECTROLYTE
LOW pH
$CO_2(g)$
$H^+$
$HCO_3^-$
HIGH pH
LOW pH
HIGH pH
82
HC3
84
HC4
83
CAS
(NEUTRALITY TO ALKALINITY)

FIG. 8

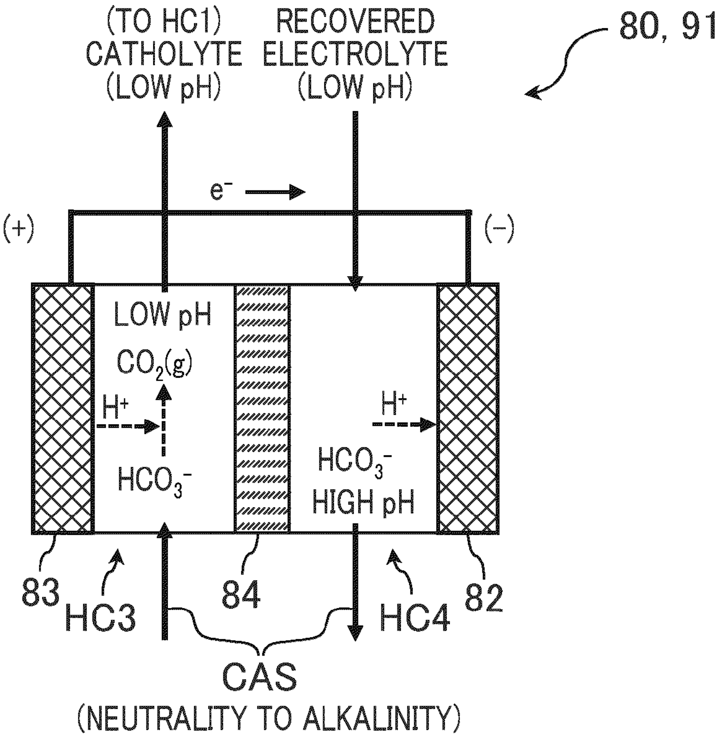
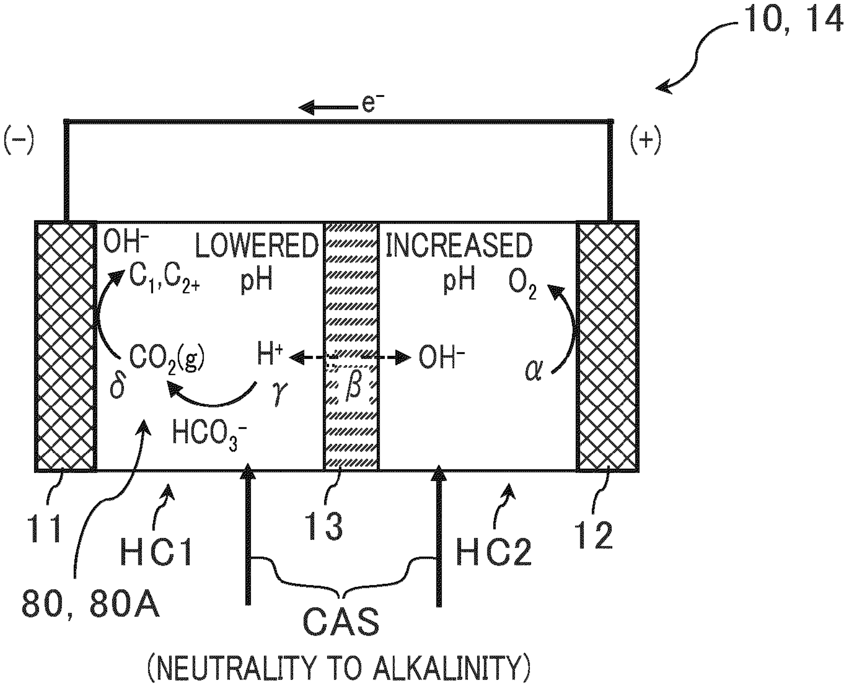
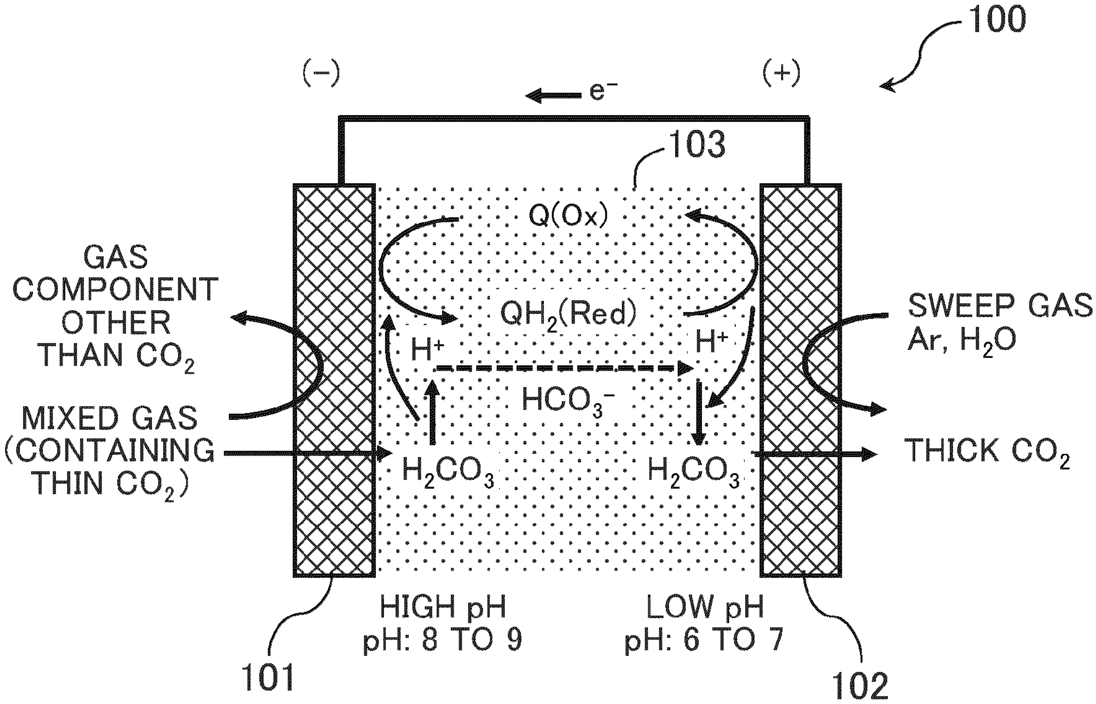

(TO HC1)
CATHOLYTE
(LOW pH)
RECOVERED
ELECTROLYTE
(LOW pH)
80, 91
$e^-$
(+)
(−)
LOW pH
$CO_2(g)$
$H^+$
$HCO_3^-$
$H^+$
$HCO_3^-$
HIGH pH
83
HC3
84
HC4
82
CAS
(NEUTRALITY TO ALKALINITY)

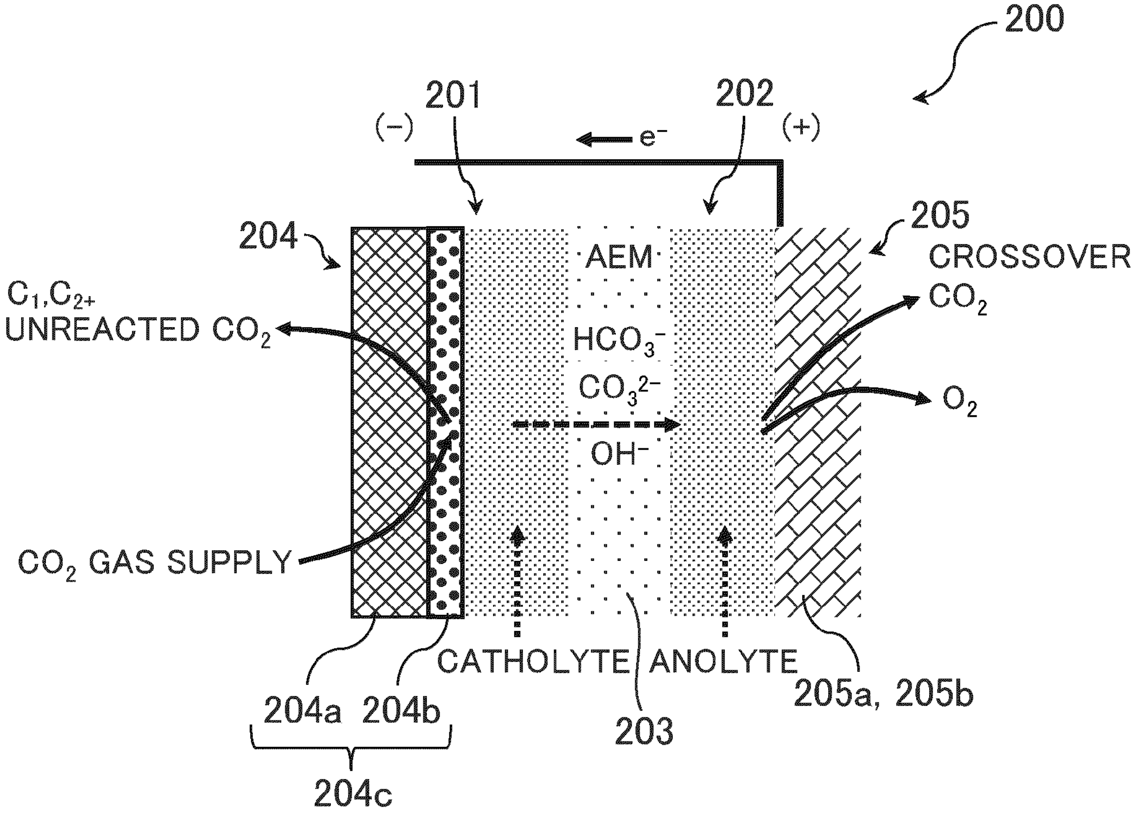
FIG. 9


10, 14
$e^-$
(−)
(+)
$OH^-$
$C_1,C_{2+}$
LOWERED
pH
INCREASED
pH
$O_2$
$CO_2(g)$
$H^+$
$OH^-$
$\delta$
$\gamma$
$\beta$
$\alpha$
$HCO_3^-$
11
HC1
13
HC2
12
80, 80A
CAS
(NEUTRALITY TO ALKALINITY)

# FIG. 10


100
(−)
(+)
e−
103
Q(Ox)
QH2(Red)
H+
H+
HCO3−
H2CO3
H2CO3
GAS COMPONENT OTHER THAN CO2
MIXED GAS (CONTAINING THIN CO2)
SWEEP GAS Ar, H2O
THICK CO2
HIGH pH pH: 8 TO 9
LOW pH pH: 6 TO 7
101
102

# FIG. 11


200
201
202
(−)
(+)
e−
204
205
CROSSOVER CO2
O2
C1,C2+ UNREACTED CO2
AEM
HCO3−
CO32−
OH−
CO2 GAS SUPPLY
CATHOLYTE
ANOLYTE
204a
204b
204c
203
205a, 205b

## REFERENCES CITED IN THE DESCRIPTION

### Patent documents cited in the description

- JP 2021147679 A **[0009] [0011]**