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(54) **CARBON DIOXIDE ELECTROLYTIC DEVICE**

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(57) **ABSTRACT**

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A carbon dioxide electrolytic device of an embodiment includes: an anode part including an anode which oxidizes water or hydroxide ions to produce oxygen; a cathode part including a cathode which reduces carbon dioxide to produce a carbon compound, a cathode solution flow path which supplies a cathode solution to the cathode, and a gas flow path which supplies carbon dioxide to the cathode; a separator which separates the anode part and the cathode part; and a differential pressure control unit which controls a differential pressure between a pressure of the cathode solution and a pressure of the carbon dioxide so as to adjust a production amount of the carbon dioxide produced by a reduction reaction in the cathode part.

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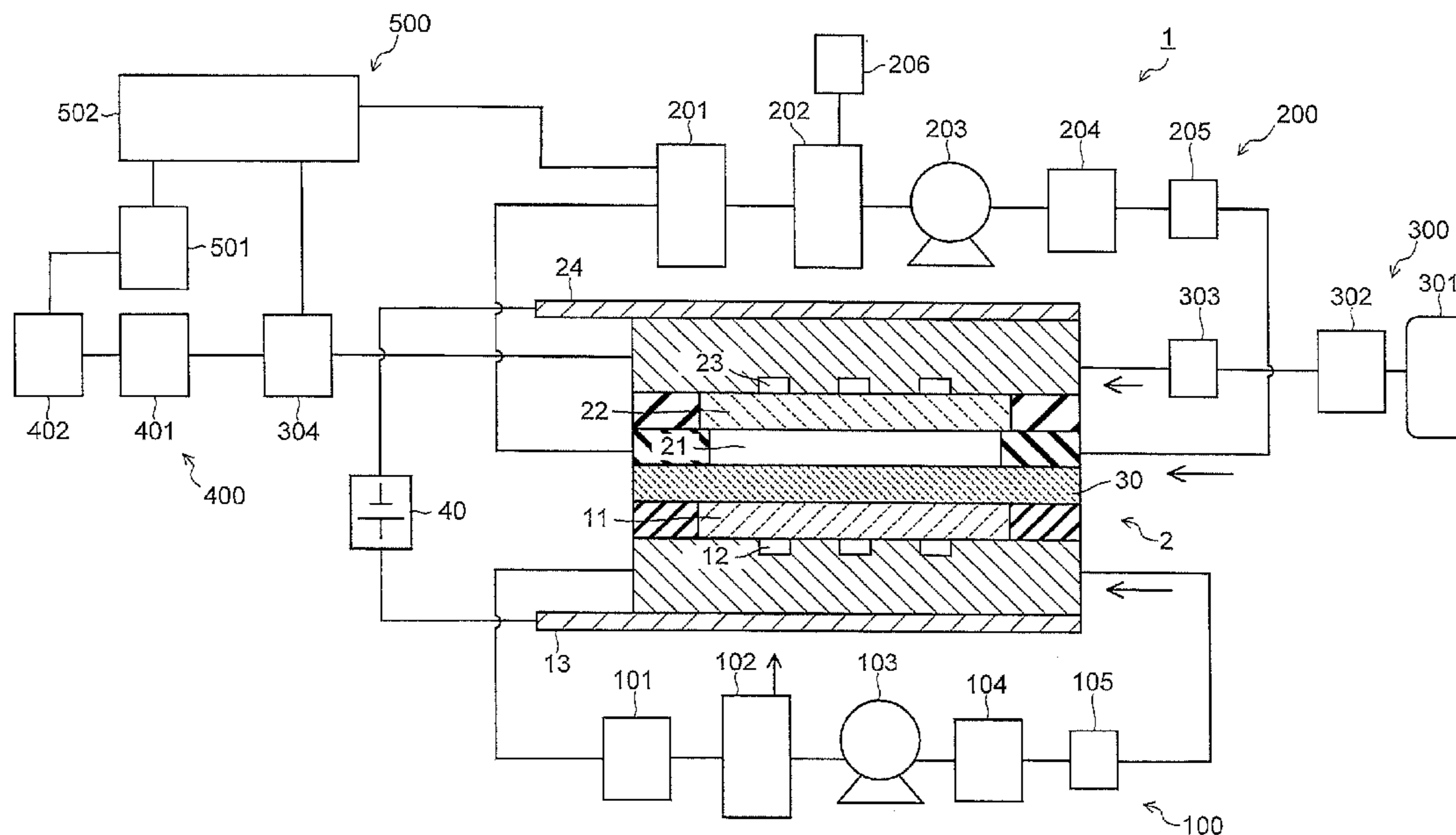


FIG. 1

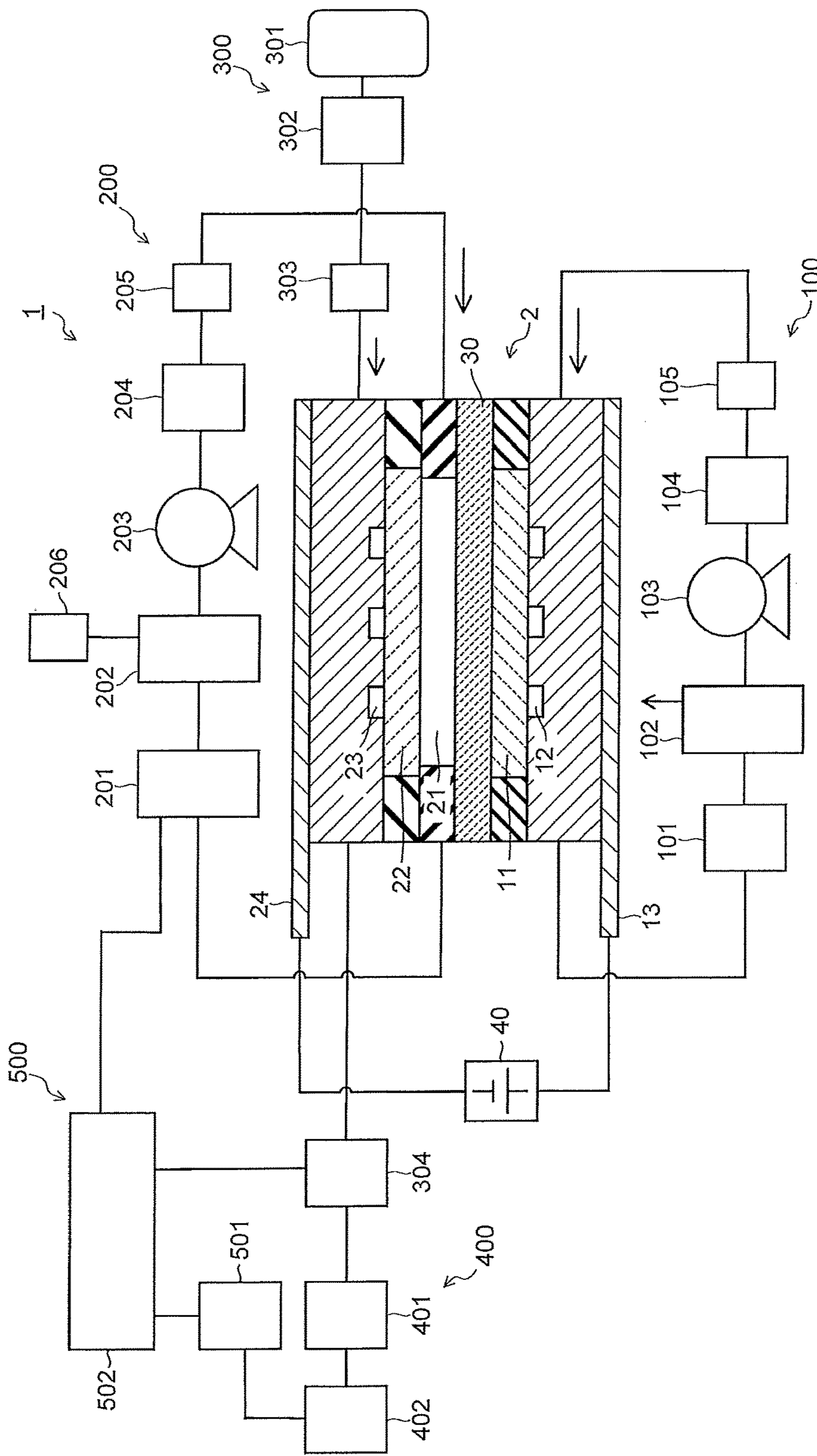


FIG. 2

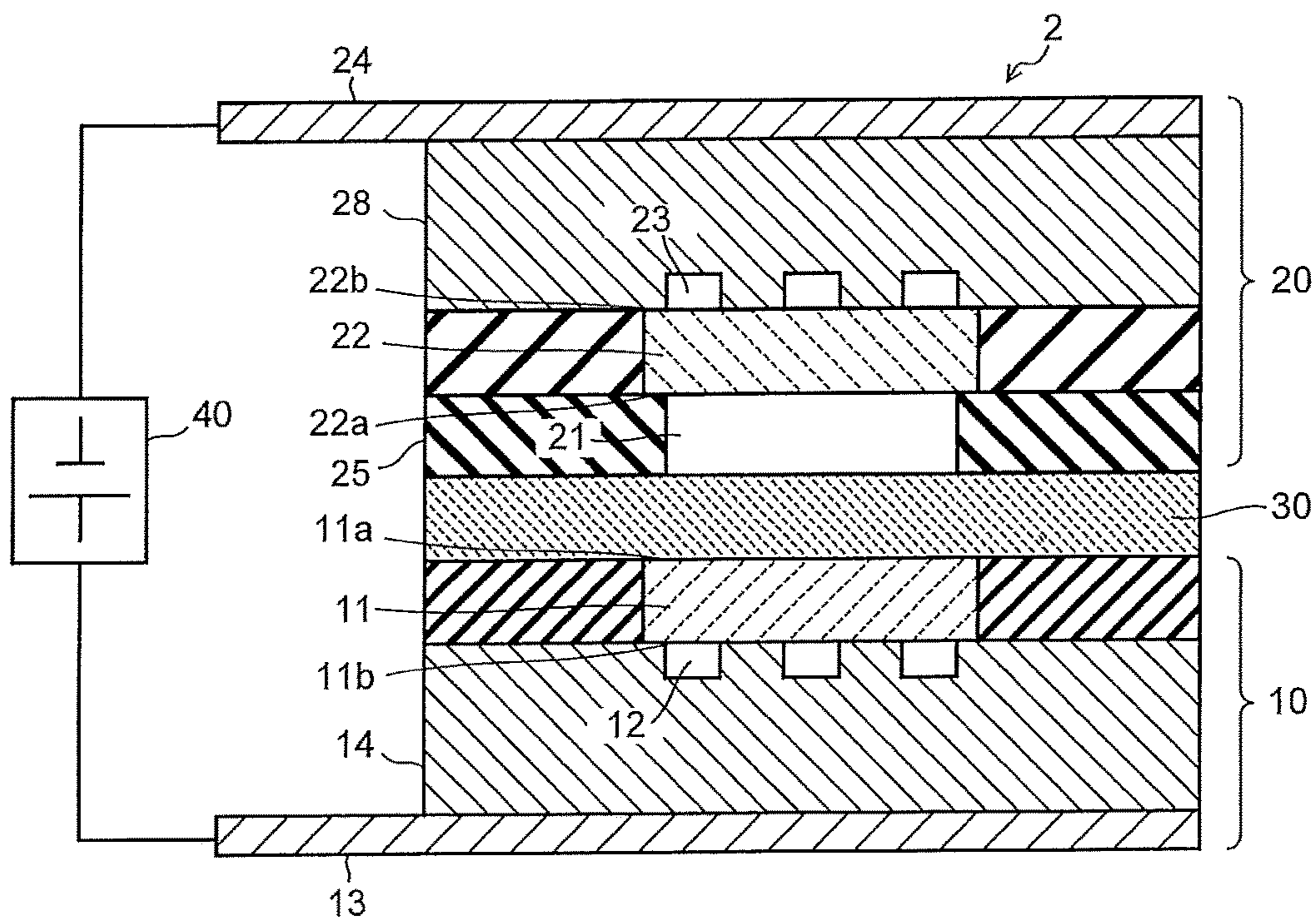


FIG. 3

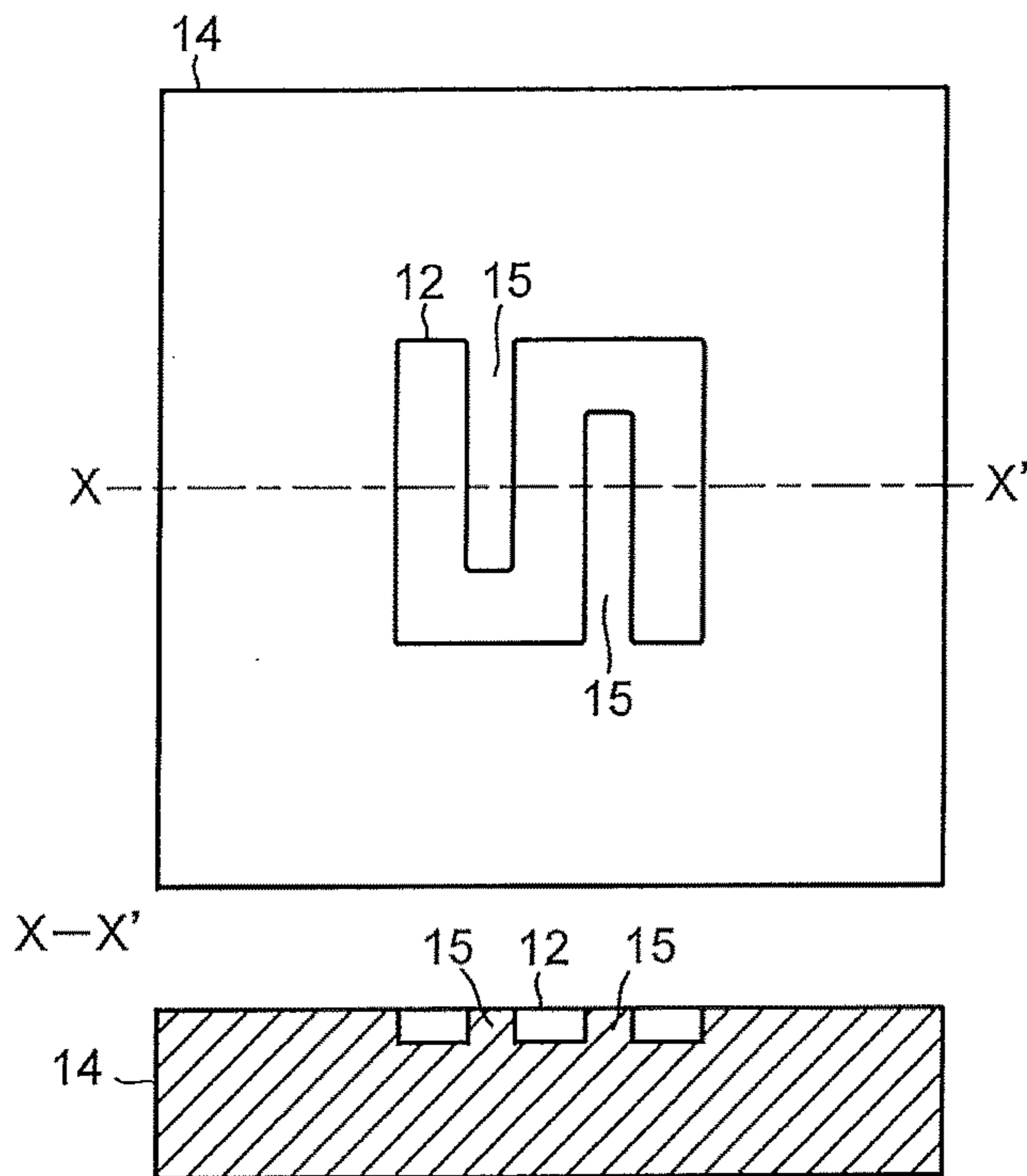


FIG. 4

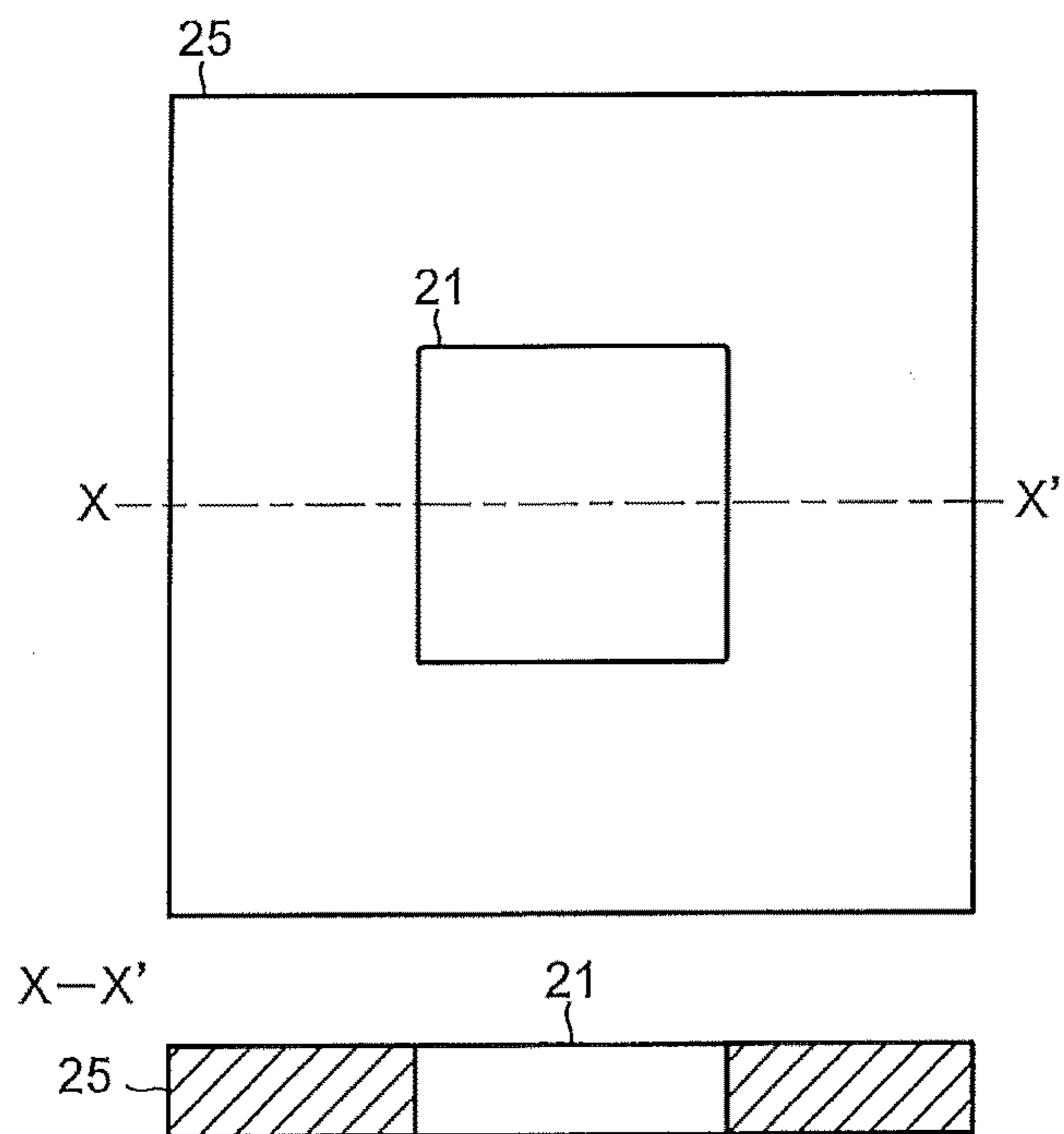


FIG. 5

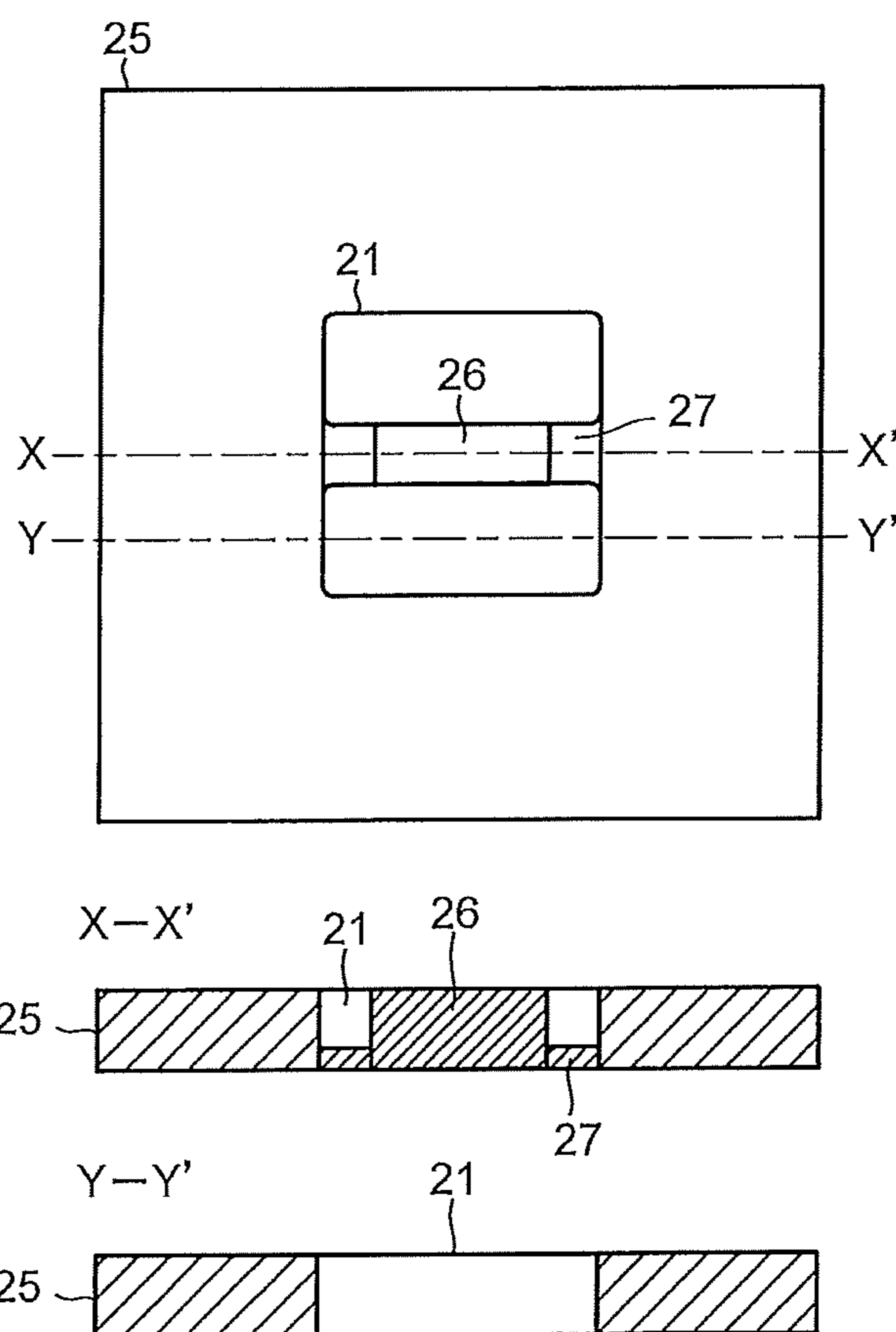


FIG. 6

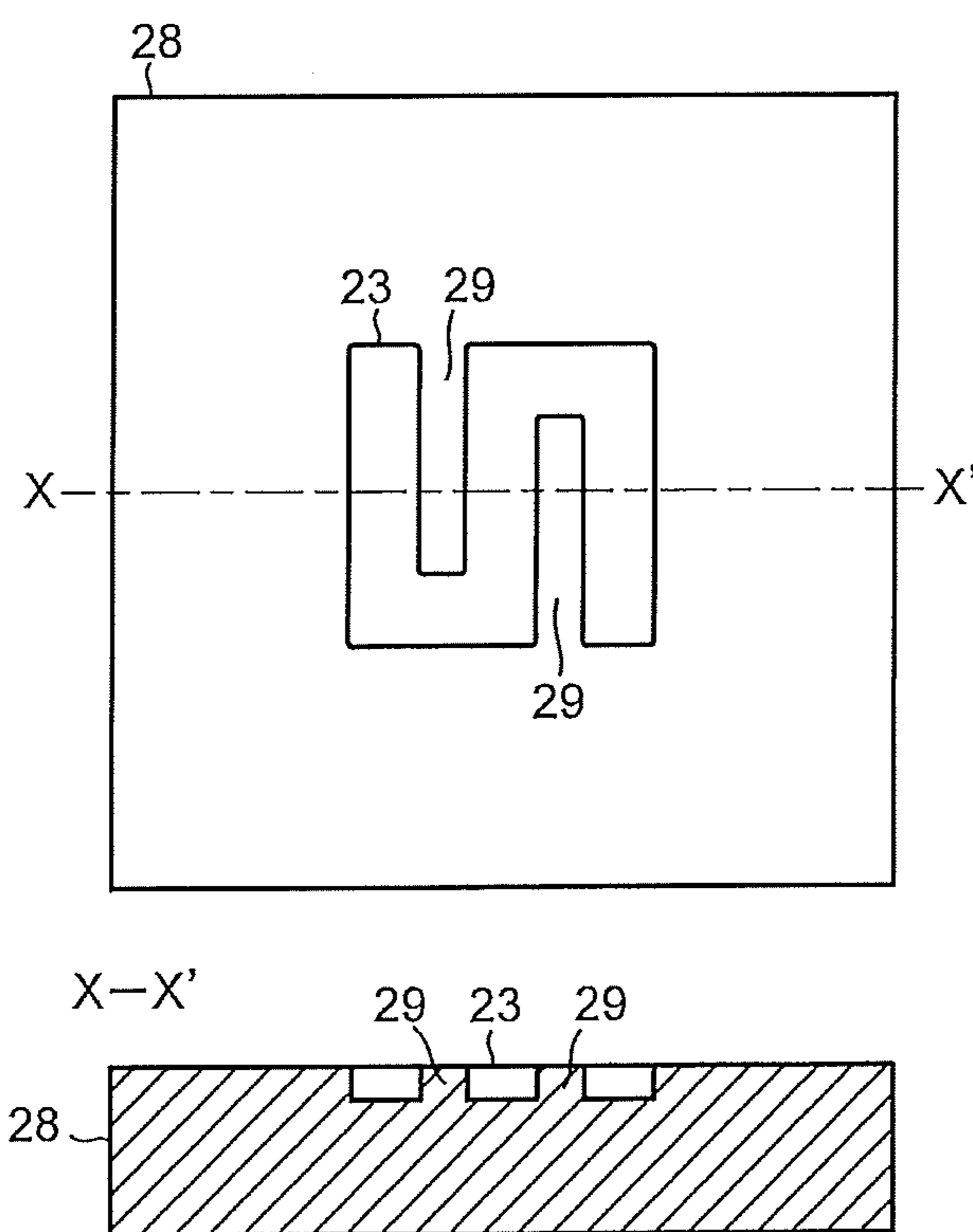


FIG. 7

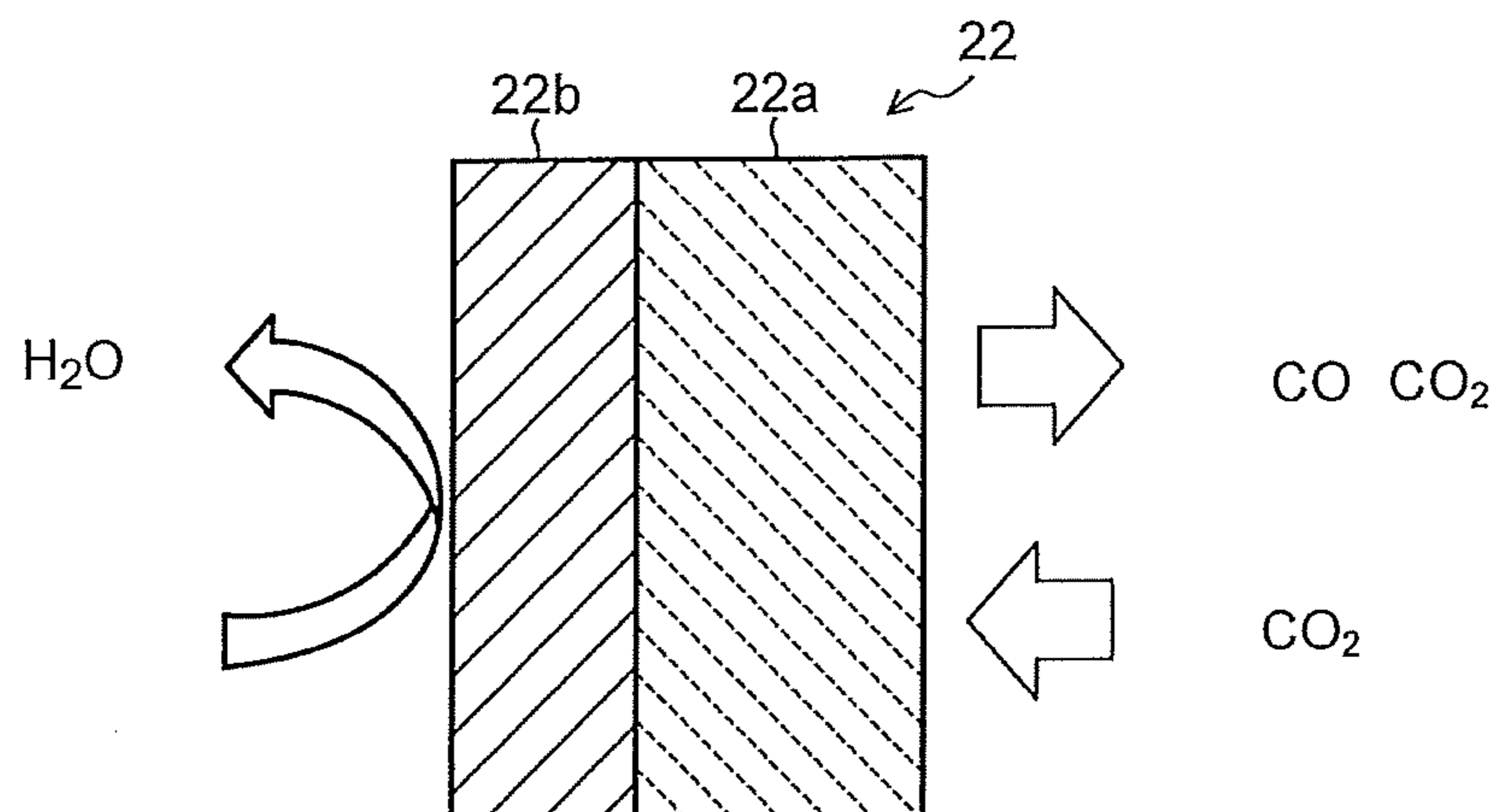


FIG. 8

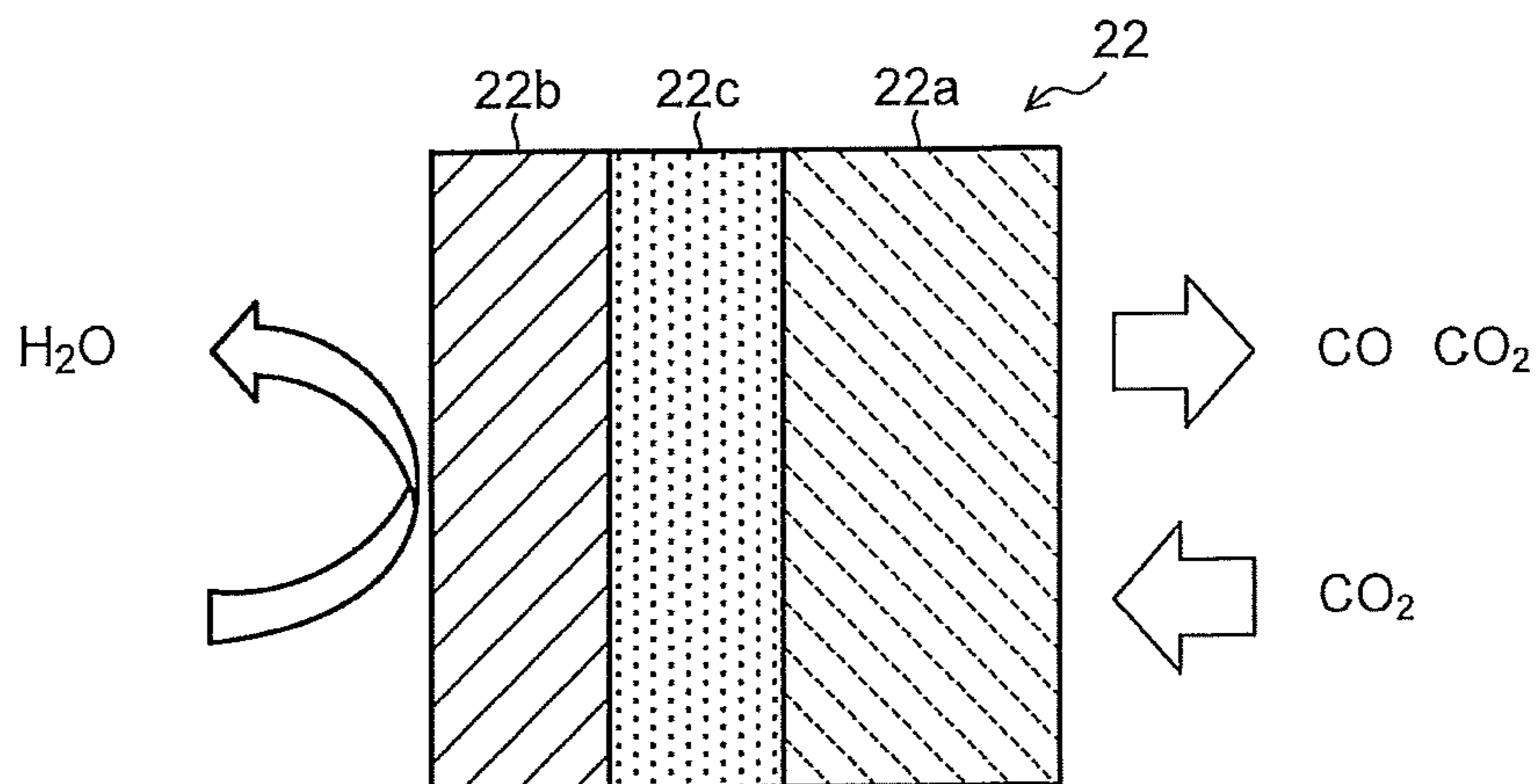


FIG. 9

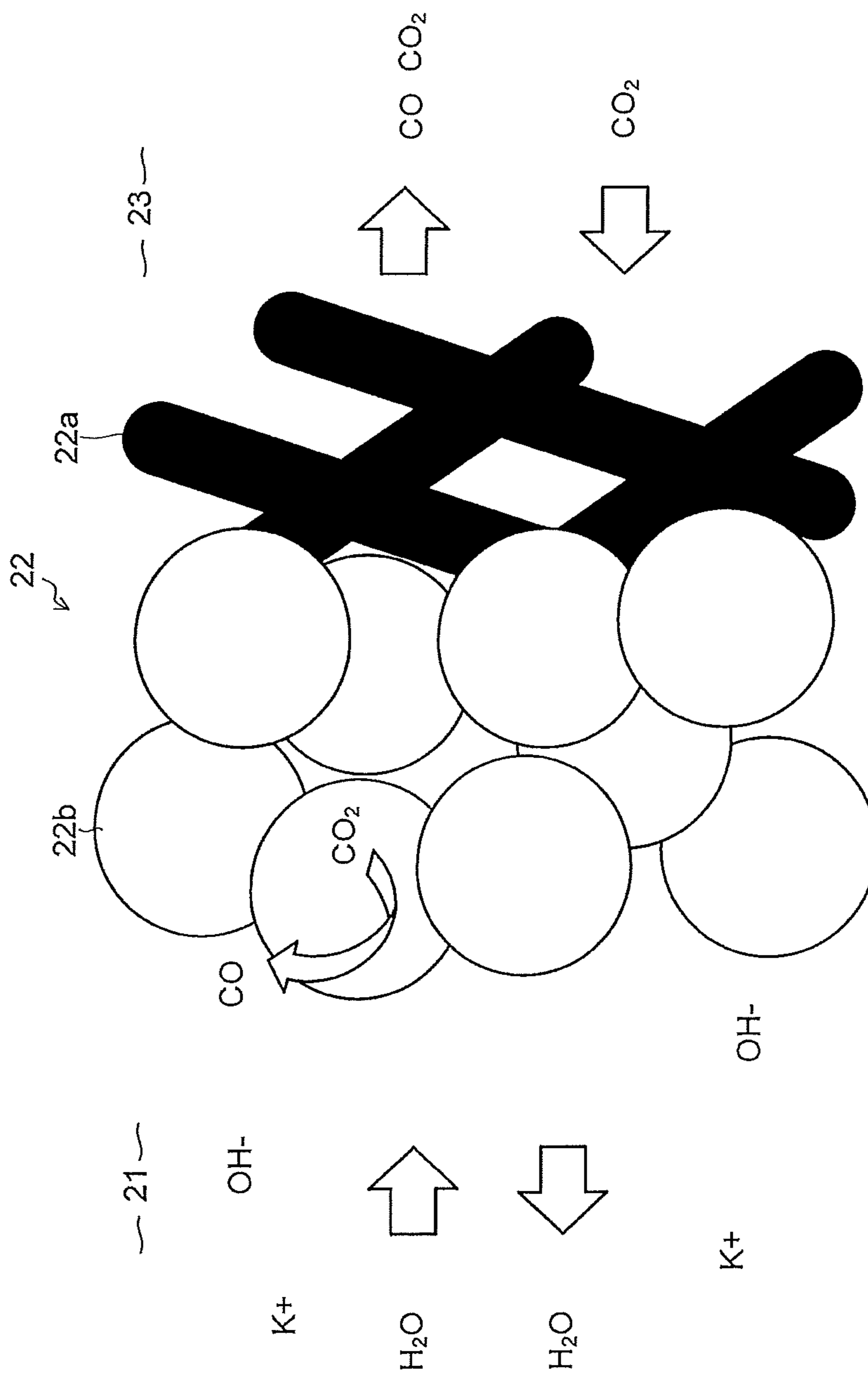
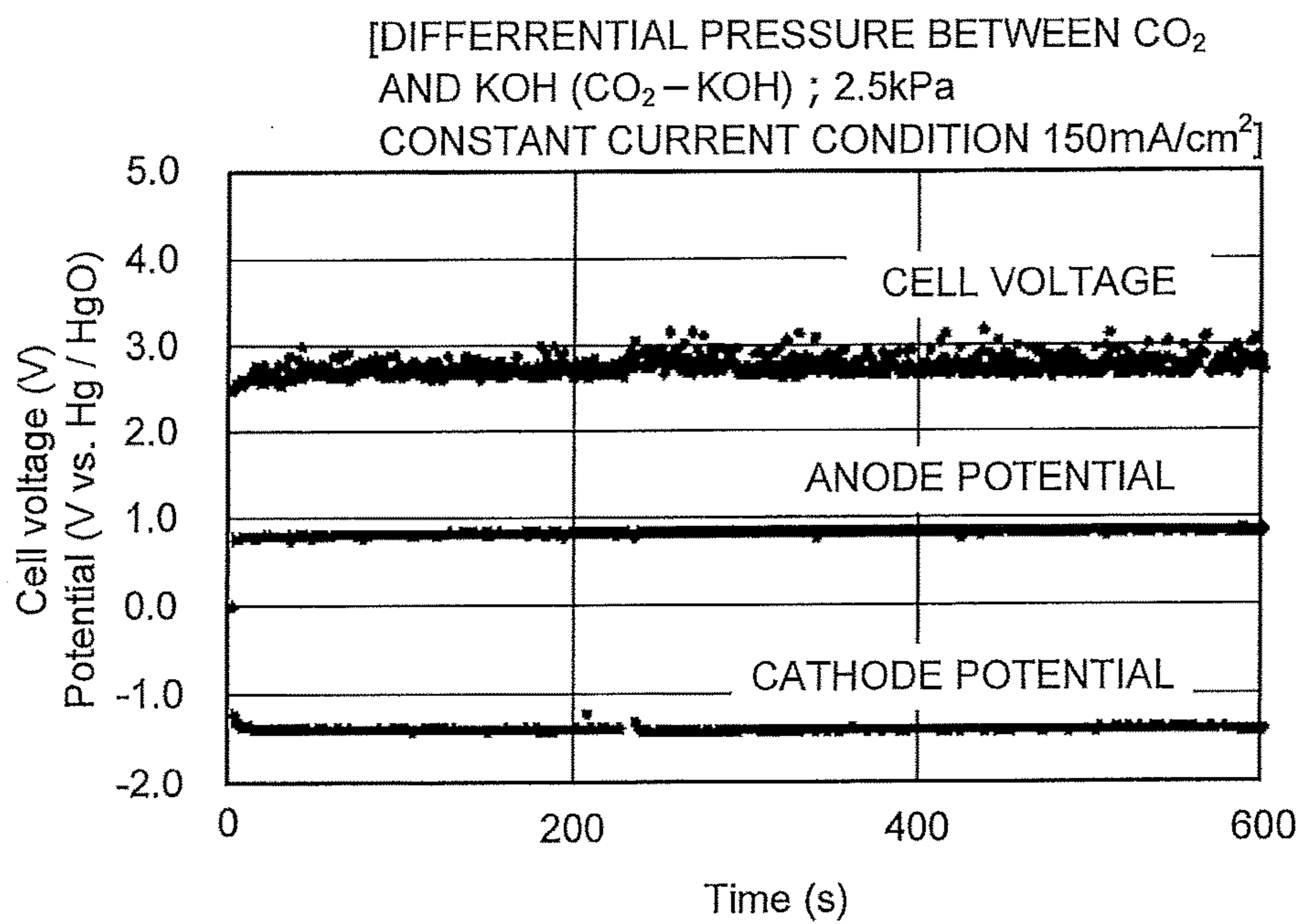




FIG. 10



## CARBON DIOXIDE ELECTROLYTIC DEVICE

### CROSS REFERENCE TO RELATED APPLICATION

[0001] This application is based upon and claims the benefit of priority from Japanese Patent Application No. 2017-048928, filed on Mar. 14, 2017; the entire contents of which are incorporated herein by reference.

### FIELD

[0002] Embodiments described herein relate generally to a carbon dioxide electrolytic device.

### BACKGROUND

[0003] In recent years, there has been a concern for depletion of fossil fuel such as petroleum or coal, and expectation for sustainably-usable renewable energy has been rising. As the renewable energy, a solar cell, wind power generation, and the like can be cited. Because these depend on weather and a natural situation in a power generation amount, there is a problem that stable supply of electric power is difficult. Therefore, there has been made an attempt to store the electric power generated by the renewable energy in a storage battery and stabilize the electric power. However, when the electric power is stored, there are problems that a cost is required for the storage battery and a loss occurs at a time of storage.

[0004] For such points, attention is being given to a technology of performing water electrolysis using the electric power generated by the renewable energy to produce hydrogen ( $H_2$ ) from water or reducing carbon dioxide ( $CO_2$ ) electrochemically to convert it into a chemical substance (chemical energy) such as a carbon compound such as carbon monoxide (CO), a formic acid (HCOOH), methanol ( $CH_3OH$ ), methane ( $CH_4$ ), an acetic acid ( $CH_3COOH$ ), ethanol ( $C_2H_5OH$ ), ethane ( $C_2H_6$ ), or ethylene ( $C_2H_4$ ). When these chemical substances are stored in a cylinder or a tank, as compared with when the electric power (electric energy) is stored in the storage battery, there are advantages that a storage cost of energy can be reduced and a storage loss is also small.

[0005] As a configuration of a carbon dioxide electrolytic device, for example, three configurations indicated below are being studied. As a first configuration, there can be cited a configuration which includes an electrolytic bath accommodating an electrolytic solution in which carbon dioxide ( $CO_2$ ) has been absorbed, an anode (oxidation electrode) and a cathode (reduction electrode) immersed in the electrolytic solution, and a separator such as an ion exchange membrane disposed so as to separate the anode and the cathode. As a second configuration, there can be cited a configuration which includes a cathode solution flow path disposed along one surface of a cathode, a  $CO_2$  gas flow path disposed along the other surface of the cathode, an anode solution flow path disposed along one surface of an anode, and a separator disposed between the cathode solution flow path and the anode solution flow path. As a third configuration, similarly to a solid polymer fuel cell, there can be cited a configuration in which an ion exchange membrane is disposed between an anode and a cathode and a  $CO_2$  gas flow path is disposed along the other surface of the cathode.

[0006] Among the above-described configuration examples of the carbon dioxide electrolytic device, in the first configuration example, in an electrolysis operation at about  $10 \text{ mA/cm}^2$  or more, an overvoltage loss is large, resulting in a large cell voltage, and therefore there is a problem that electrolysis efficiency at a high current density is low. In the second configuration example, a cell voltage can be reduced more than that in the first configuration example, and the electrolysis efficiency can be improved. However, there is a problem that selectivity of a product to be obtained by a reduction reaction on a cathode side is low and variations exist in the electrolysis efficiency in the second configuration example. Note that in the third configuration example, development, selection, and the like of an ion exchange membrane suitable for electrolysis of  $CO_2$  are required.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0007] FIG. 1 is a view illustrating a carbon dioxide electrolytic device of an embodiment.

[0008] FIG. 2 is a sectional view illustrating an electrolysis cell of the carbon dioxide electrolytic device illustrated in FIG. 1.

[0009] FIG. 3 is a view illustrating one example of an anode solution flow path in the electrolysis cell illustrated in FIG. 2.

[0010] FIG. 4 is a view illustrating one example of a cathode solution flow path in the electrolysis cell illustrated in FIG. 2.

[0011] FIG. 5 is a view illustrating the other example of the cathode solution flow path in the electrolysis cell illustrated in FIG. 2.

[0012] FIG. 6 is a view illustrating one example of a  $CO_2$  gas flow path in the electrolysis cell illustrated in FIG. 2.

[0013] FIG. 7 is a view illustrating one example of a cathode in the electrolysis cell illustrated in FIG. 2.

[0014] FIG. 8 is a view illustrating the other example of the cathode in the electrolysis cell illustrated in FIG. 2.

[0015] FIG. 9 is a view schematically illustrating a reaction in the cathode in the electrolysis cell illustrated in FIG. 2.

[0016] FIG. 10 is a chart illustrating time changes in a cell voltage, an anode potential, and a cathode potential by using a carbon dioxide electrolytic device in an example.

### DETAILED DESCRIPTION

[0017] According to the embodiments of the present invention, there is provided a carbon dioxide electrolytic device that includes: a cathode part including a cathode to reduce carbon dioxide and thus produce a carbon compound, a cathode solution flow path to supply a cathode solution to the cathode, and a gas flow path to supply carbon dioxide to the cathode; an anode part including an anode to oxidize water or hydroxide ions and thus produce oxygen and an anode solution flow path to supply an anode solution to the anode; a separator to separate the anode part and the cathode part; a power supply to pass an electric current between the anode and the cathode; a first pressure control unit to control a pressure of the cathode solution flowing in the cathode solution flow path; a second pressure control unit to control a pressure of the carbon dioxide flowing in the gas flow path; a detection unit to detect a production amount of the carbon compound produced by a reduction reaction in the cathode

part; and a differential pressure control unit to control a differential pressure between a pressure of the cathode solution and a pressure of the carbon dioxide so as to adjust the production amount of the carbon compound detected in the detection unit.

[0018] Hereinafter, a carbon dioxide electrolytic device of an embodiment will be described with reference to the drawings. In the embodiment presented below, substantially the same components are denoted by the same reference signs, and a description thereof is sometimes partially omitted. The drawings are schematic, and a relationship between a thickness and a planar size, thickness proportions of the respective portions, and the like are sometimes different from actual ones.

[0019] FIG. 1 is a view illustrating a configuration of a carbon dioxide electrolytic device according to the embodiment. FIG. 2 is a sectional view illustrating a configuration of an electrolysis cell in the electrolytic device illustrated in FIG. 1. A carbon dioxide electrolytic device 1 illustrated in FIG. 1 includes: an electrolysis cell 2; an anode solution supply system 100 which supplies an anode solution to the electrolysis cell 2; a cathode solution supply system 200 which supplies a cathode solution to the electrolysis cell 2; a gas supply system 300 which supplies carbon dioxide ( $\text{CO}_2$ ) gas to the electrolysis cell 2; a product collection system 400 which collects a product produced by a reduction reaction in the electrolysis cell 2; and a product control system 500 which detects a type and a production amount of the collected product and controls the product.

[0020] The electrolysis cell 2 includes an anode part 10, a cathode part 20, and a separator 30 as illustrated in FIG. 2. The anode part 10 includes an anode 11, an anode solution flow path 12, and an anode current collector 13. The cathode part 20 includes a cathode solution flow path 21, a cathode 22, a  $\text{CO}_2$  gas flow path 23, and a cathode current collector 24. The separator 30 is disposed so as to separate the anode part 10 and the cathode part 20. The electrolysis cell 2 is sandwiched by a pair of support plates not illustrated, and further tightened by bolts or the like. In FIG. 1 and FIG. 2, a reference sign 40 is a power supply which passes an electric current through the anode 11 and the cathode 22. The power supply 40 is connected via a current introduction member to the anode 11 and the cathode 22. The power supply 40 is not limited to a normal commercial power supply, battery, or the like, and may supply electric power generated by renewable energy such as a solar cell or wind power generation.

[0021] The anode 11 is an electrode (oxidation electrode) which causes an oxidation reaction of water ( $\text{H}_2\text{O}$ ) in an anode solution to produce oxygen ( $\text{O}_2$ ) or hydrogen ions ( $\text{H}^+$ ), or causes an oxidation reaction of hydroxide ions ( $\text{OH}^-$ ) produced in the cathode part 20 to produce oxygen ( $\text{O}_2$ ) or water ( $\text{H}_2\text{O}$ ). The anode 11 preferably has a first surface 11a in contact with the separator 30 and a second surface 11b facing the anode solution flow path 12. The first surface 11a of the anode 11 is in close contact with the separator 30. The anode solution flow path 12 supplies the anode solution to the anode 11, and is constituted by a pit (groove portion/concave portion) provided in a first flow path plate 14. The anode solution flows through in the anode solution flow path 12 so as to be in contact with the anode 11. The anode current collector 13 is electrically in contact

with a surface on a side opposite to the anode 11 of the first flow path plate 14 constituting the anode solution flow path 12.

[0022] To the first flow path plate 14, a solution inlet port and a solution outlet port whose illustrations are omitted are connected, and via these solution inlet port and solution outlet port, the anode solution is introduced and discharged by the anode solution supply system 100. For the first flow path plate 14, a material having low chemical reactivity and high conductivity is preferably used. As such a material, a metal material such as Ti or SUS, carbon, or the like can be cited. Along the anode solution flow path 12, as illustrated in FIG. 3, a plurality of lands (convex portions) 15 are preferably provided. The lands 15 are provided for mechanical retention and electrical continuity. The lands 15 are preferably provided alternately to uniformize flow of the anode solution. The above lands 15 make the anode solution flow path 12 serpentine. Moreover, also for a good discharge of the anode solution in which oxygen ( $\text{O}_2$ ) gas is mixed, the lands 15 are preferably provided alternately along the anode solution flow path 12 to make the anode solution flow path 12 serpentine.

[0023] The anode 11 is preferably mainly constituted of a catalyst material (anode catalyst material) capable of oxidizing water ( $\text{H}_2\text{O}$ ) to produce oxygen or hydrogen ions or oxidizing hydroxide ions ( $\text{OH}^-$ ) to produce water or oxygen, and capable of reducing an overvoltage of the above reaction. As such a catalyst material, there can be cited a metal such as platinum (Pt), palladium (Pd), or nickel (Ni), an alloy or an intermetallic compound containing the above metals, a binary metal oxide such as a manganese oxide ( $\text{Mn—O}$ ), an iridium oxide ( $\text{Ir—O}$ ), a nickel oxide ( $\text{Ni—O}$ ), a cobalt oxide ( $\text{Co—O}$ ), an iron oxide ( $\text{Fe—O}$ ), a tin oxide ( $\text{Sn—O}$ ), an indium oxide ( $\text{In—O}$ ), a ruthenium oxide ( $\text{Ru—O}$ ), a lithium oxide ( $\text{Li—O}$ ), or a lanthanum oxide ( $\text{La—O}$ ), a ternary metal oxide such as  $\text{Ni—Co—O}$ ,  $\text{Ni—Fe—O}$ ,  $\text{La—Co—O}$ ,  $\text{Ni—La—O}$ , or  $\text{Sr—Fe—O}$ , a quaternary metal oxide such as  $\text{Pb—Ru—Ir—O}$  or  $\text{La—Sr—Co—O}$ , or a metal complex such as a Ru complex or a Fe complex.

[0024] The anode 11 includes a base material having a structure capable of moving the anode solution or ions between the separator 30 and the anode solution flow path 12, for example, a porous structure such as a mesh material, a punching material, a porous body, or a metal fiber sintered body. The base material may be constituted of a metal such as titanium (Ti), nickel (Ni), or iron (Fe), or a metal material such as an alloy (for example, SUS) containing at least one of these metals, or may be constituted of the above-described anode catalyst material. When the oxide is used as the anode catalyst material, the anode catalyst material preferably adheres to or is stacked on a surface of the base material constituted of the above-described metal material to form a catalyst layer. The anode catalyst material preferably has nanoparticles, a nanostructure, a nanowire, or the like for the purpose of increasing the oxidation reaction. The nanostructure is a structure in which nanoscale irregularities are formed on a surface of the catalyst material.

[0025] The cathode 22 is an electrode (reduction electrode) which causes a reduction reaction of carbon dioxide ( $\text{CO}_2$ ) or a reduction reaction of a carbon compound produced thereby to produce a carbon compound such as carbon monoxide (CO), methane ( $\text{CH}_4$ ), ethane ( $\text{C}_2\text{H}_6$ ), ethylene ( $\text{C}_2\text{H}_4$ ), methanol ( $\text{CH}_3\text{OH}$ ), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), or ethylene

glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>). In the cathode **22**, simultaneously with the reduction reaction of carbon dioxide (CO<sub>2</sub>), a side reaction in which hydrogen (H<sub>2</sub>) is produced by a reduction reaction of water (H<sub>2</sub>O) is sometimes caused. The cathode **22** has a first surface **22a** facing the cathode solution flow path **21** and a second surface **22b** facing the CO<sub>2</sub> gas flow path **23**. The cathode solution flow path **21** is disposed between the cathode **22** and the separator **30** so that the cathode solution is in contact with the cathode **22** and the separator **30**.

[0026] The cathode solution flow path **21** is constituted by an opening portion provided in a second flow path plate **25**. To the second flow path plate **25**, a solution inlet port and a solution outlet port whose illustrations are omitted are connected, and via these solution inlet port and solution outlet port, the cathode solution is introduced and discharged by the cathode solution supply system **200**. The cathode solution flows through in the cathode solution flow path **21** so as to be in contact with the cathode **22** and the separator **30**. For the second flow path plate **25** constituting the cathode solution flow path **21**, a material having low chemical reactivity and having no conductivity is preferably used. As such a material, there can be cited an insulating resin material such as an acrylic resin, polyetheretherketone (PEEK), or a fluorocarbon resin.

[0027] In the cathode **22**, the reduction reaction of CO<sub>2</sub> occurs mainly in a portion in contact with the cathode solution. Therefore, to the cathode solution flow path **21**, as illustrated in FIG. 4, the opening portion having a large opening area is preferably applied. However, in order to enhance mechanical retention and electrical connectivity, as illustrated in FIG. 5, a land (convex portion) **26** may be provided in the cathode solution flow path **21**. The land **26** in the cathode solution flow path **21** is provided in a center portion of the cathode solution flow path **21**, and is retained to the second flow path plate **25** by a bridge portion **27** thinner than the land **26** by so as not to prevent the cathode solution in the cathode solution flow path **21** from flowing through. When the land **26** is provided in the cathode solution flow path **21**, the number of lands **26** is preferably small in order to reduce cell resistance.

[0028] The CO<sub>2</sub> gas flow path **23** is constituted by a pit (groove portion/concave portion) provided in a third flow path plate **28**. For the third flow path plate **28** constituting the CO<sub>2</sub> gas flow path, a material having low chemical reactivity and high conductivity is preferably used. As such a material, the metal material such as Ti or SUS, carbon, or the like can be cited. Note that in each of the first flow path plate **14**, the second flow path plate **25**, and the third flow path plate **28**, an inlet port and an outlet port for a solution or gas, screw holes for tightening, and the like, whose illustrations are omitted, are provided. Further, in front of and behind each of the flow path plates **14**, **25**, and **28**, packing whose illustration is omitted is sandwiched as necessary.

[0029] To the third flow path plate **28**, a gas inlet port and a gas outlet port whose illustrations are omitted are connected, and via these gas inlet port and gas outlet port, CO<sub>2</sub> gas or gas containing CO<sub>2</sub> (sometimes collectively referred to simply as CO<sub>2</sub> gas) is introduced and discharged by the gas supply system **300**. The CO<sub>2</sub> gas flows through in the CO<sub>2</sub> gas flow path **23** so as to be in contact with the cathode **22**. Along the CO<sub>2</sub> gas flow path **23**, as illustrated in FIG. 6, a plurality of lands (convex portions) **29** are preferably provided. The lands **29** are provided for the mechanical retention and the electrical continuity. The lands **29** are

preferably provided alternately, and this makes the CO<sub>2</sub> gas flow path **23** serpentine similarly to the anode solution flow path **12**. The cathode current collector **24** is electrically in contact with a surface on a side opposite to the cathode **22** of the third flow path plate **28**.

[0030] The cathode **22** has a gas diffusion layer **22a** and a cathode catalyst layer **22b** provided thereon as illustrated in FIG. 7. Between the gas diffusion layer **22a** and the cathode catalyst layer **22b**, as illustrated in FIG. 8, a porous layer **22c** denser than the gas diffusion layer **22a** may be disposed. As illustrated in FIG. 9, the gas diffusion layer **22a** is disposed on the CO<sub>2</sub> gas flow path **23** side, and the cathode catalyst layer **22b** is disposed on the cathode solution flow path **21** side. The cathode catalyst layer **22b** preferably has catalyst nanoparticles, a catalyst nanostructure, or the like. The gas diffusion layer **22a** is constituted by carbon paper, carbon cloth, or the like, for example, and subjected to water repellent treatment. The porous layer **22c** is constituted by a porous body whose pore size is smaller than that of the carbon paper or the carbon cloth.

[0031] As illustrated in a schematic view in FIG. 9, in the cathode catalyst layer **22b**, the cathode solution or ions are supplied and discharged from the cathode solution flow path **21**, and in the gas diffusion layer **22a**, the CO<sub>2</sub> gas is supplied from the CO<sub>2</sub> gas flow path **23** and further a product by the reduction reaction of the CO<sub>2</sub> gas is discharged. By subjecting the gas diffusion layer **22a** to moderate water repellent treatment, the CO<sub>2</sub> gas reaches the cathode catalyst layer **22b** mainly owing to gas stirring. The reduction reaction of CO<sub>2</sub> or the reduction reaction of a carbon compound produced thereby occurs in the vicinity of a boundary between the gas diffusion layer **22a** and the cathode catalyst layer **22b**, a gaseous product is discharged mainly from the CO<sub>2</sub> gas flow path **23**, and a liquid product is discharged mainly from the cathode solution flow path **21**.

[0032] The cathode catalyst layer **22b** is preferably constituted of a catalyst material (cathode catalyst material) capable of reducing carbon dioxide to produce a carbon compound and further reducing the carbon compound produced thereby to produce a carbon compound as necessary, and capable of reducing an overvoltage of the above reaction. As such a material, there can be cited a metal such as gold (Au), silver (Ag), copper (Cu), platinum (Pt), palladium (Pd), nickel (Ni), cobalt (Co), iron (Fe), manganese (Mn), titanium (Ti), cadmium (Cd), zinc (Zn), indium (In), gallium (Ga), lead (Pb), or tin (Sn), a metal material such as an alloy or an intermetallic compound containing at least one of the above metals, a carbon material such as carbon (C), graphene, CNT (carbon nanotube), fullerene, or ketjen black, or a metal complex such as a Ru complex or a Re complex. To the cathode catalyst layer **22b**, various shapes such as a plate shape, a mesh shape, a wire shape, a particle shape, a porous shape, a thin film shape, and an island shape can be applied.

[0033] The cathode catalyst material constituting the cathode catalyst layer **22b** preferably has nanoparticles of the above-described metal material, a nanostructure of the metal material, nanowires of the metal material, or a composite body in which the nanoparticles of the above-described metal material are supported by a carbon material such as carbon particles, carbon nanotubes, or graphene. Applying catalyst nanoparticles, a catalyst nanostructure, a catalyst nanowire, a catalyst nano-support structure, or the like as the

cathode catalyst material makes it possible to enhance reaction efficiency of the reduction reaction of carbon dioxide in the cathode 22.

[0034] The separator 30 is constituted of an ion exchange membrane or the like capable of moving ions between the anode 11 and the cathode 22 and separating the anode part 10 and the cathode part 20. As the ion exchange membrane, for example, a cation exchange membrane such as Nafion or Flemion, or an anion exchange membrane such as Neosepta, or Selemion can be used. As described later, when an alkaline solution is used as the anode solution or the cathode solution and it is assumed that hydroxide ions ( $\text{OH}^-$ ) move mainly, the separator 30 is preferably constituted of the anion exchange membrane. Also other than the ion exchange membrane, a glass filter, a porous polymeric membrane, a porous insulating material, or the like may be applied to the separator 30 as long as they are a material capable of moving ions between the anode 11 and the cathode 22.

[0035] The anode solution and the cathode solution are preferably a solution containing at least water ( $\text{H}_2\text{O}$ ). Because carbon dioxide ( $\text{CO}_2$ ) is supplied from the  $\text{CO}_2$  gas flow path 23, the cathode solution may contain or need not contain carbon dioxide ( $\text{CO}_2$ ). To the anode solution and the cathode solution, the same solution may be applied or different solutions may be applied. As a solution used as the anode solution and the cathode solution and containing  $\text{H}_2\text{O}$ , for example, an aqueous solution containing an arbitrary electrolyte can be cited. As the aqueous solution containing the electrolyte, for example, there can be cited an aqueous solution containing at least one ion selected from a hydroxide ion ( $\text{OH}^-$ ), a hydrogen ion ( $\text{H}^+$ ), a potassium ion ( $\text{K}^+$ ), a sodium ion ( $\text{Na}^+$ ), a lithium ion ( $\text{Li}^+$ ), a chloride ion ( $\text{Cl}^-$ ), a bromide ion ( $\text{Br}^-$ ), an iodide ion ( $\text{I}^-$ ), a nitrate ion ( $\text{NO}_3^-$ ), a sulfate ion ( $\text{SO}_4^{2-}$ ), a phosphate ion ( $\text{PO}_4^{2-}$ ), a borate ion ( $\text{BO}_3^{3-}$ ), and a hydrogen carbonate ion ( $\text{HCO}_3^-$ ). In order to reduce electrical resistance of the solution, as the anode solution and the cathode solution, an alkaline solution in which an electrolyte such as a potassium hydroxide or a sodium hydroxide is dissolved in high concentration is preferably used.

[0036] For the cathode solution, an ionic liquid which is made of salts of cations such as imidazolium ions or pyridinium ions and anions such as  $\text{BF}_4^-$  or  $\text{PF}_6^-$  and which is in a liquid state in a wide temperature range, or its aqueous solution may be used. As another cathode solution, there can be cited an amine solution of ethanolamine, imidazole, pyridine, or the like, or an aqueous solution thereof. As amine, any of primary amine, secondary amine, and tertiary amine is applicable.

[0037] To the anode solution flow path 12 of the anode part 10, the anode solution is supplied from the anode solution supply system 100. The anode solution supply system 100 circulates the anode solution so that the anode solution flows through in the anode solution flow path 12. The anode solution supply system 100 has a pressure control unit 101, an anode solution tank 102, a flow rate control unit (pump) 103, a reference electrode 104, and a pressure gauge 105, and is constituted so that the anode solution circulates in the anode solution flow path 12. The anode solution tank 102 is connected to a gas component collection unit which collects a gas component such as oxygen ( $\text{O}_2$ ) contained in the circulating anode solution and is not illustrated. The anode solution, whose flow rate and pressure are controlled

in the pressure control unit 101 and the flow rate control unit 103, is introduced to the anode solution flow path 12.

[0038] To the cathode solution flow path 21 of the cathode part 20, the cathode solution is supplied from the cathode solution supply system 200. The cathode solution supply system 200 circulates the cathode solution so that the cathode solution flows through in the cathode solution flow path 21. The cathode solution supply system 200 has a pressure control unit 201, a cathode solution tank 202, a flow rate control unit (pump) 203, a reference electrode 204, and a pressure gauge 205, and is constituted so that the cathode solution circulates in the cathode solution flow path 21. The cathode solution tank 202 is connected to a gas component collection unit 206 which collects a gas component such as carbon monoxide ( $\text{CO}$ ) contained in the circulating cathode solution. The cathode solution, whose flow rate and pressure are controlled in the pressure control unit 201 and the flow rate control unit 203, is introduced to the cathode solution flow path 21.

[0039] To the  $\text{CO}_2$  gas flow path 23, the  $\text{CO}_2$  gas is supplied from the gas supply system 300. The gas supply system 300 has a  $\text{CO}_2$  gas cylinder 301, a flow rate control unit 302, a pressure gauge 303, and a pressure control unit 304. The  $\text{CO}_2$  gas, whose flow rate and pressure are controlled in the flow rate control unit 302 and the pressure control unit 304, is introduced to the  $\text{CO}_2$  gas flow path 23. The gas supply system 300 is connected to the product collection system 400 which collects a product in gas which has flowed through the  $\text{CO}_2$  gas flow path 23. The product collection system 400 has a gas/liquid separation unit 401 and a product collection unit 402. A reduction product such as  $\text{CO}$  or  $\text{H}_2$  contained in the gas which has flowed through the  $\text{CO}_2$  gas flow path 23 is accumulated via the gas/liquid separation unit 401 in the product collection unit 402.

[0040] Part of the reduction product accumulated in the product collection unit 402 is sent to a reduction performance detection unit 501 of the product control system 500. In the reduction performance detection unit 501, a production amount and a proportion of each product such as  $\text{CO}$  or  $\text{H}_2$  in the reduction product are detected. The detected production amount and proportion of each product are inputted to a data collection control unit 502 of the product control system 500. The data collection control unit 502 is electrically connected via bi-directional signal lines whose illustration is partially omitted to the pressure control unit 101 and the flow rate control unit 103 of the anode solution supply system 100, the pressure control unit 201 and the flow rate control unit 203 of the cathode solution supply system 200, and the flow rate control unit 302 and the pressure control unit 304 of the gas supply system 300 in addition to the reduction performance detection unit 501.

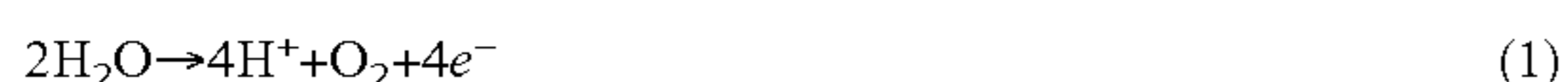
[0041] Each operation of the electrolysis cell 2, the power supply 40, the anode solution supply system 100, the cathode solution supply system 200, and the gas supply system 300 is controlled by the data collection control unit 502. That is, the data collection control unit 502 controls the pressure control unit 201 of the cathode solution supply system 200 and the pressure control unit 304 of the gas supply system 300 so as to adjust the production amount and the proportion of each product detected in the reduction performance detection unit 501, specifically so that the production amount and the proportion of each product each become a desired value. Thereby, a differential pressure between a pressure of the cathode solution flowing through the cathode

solution flow path **21** and a pressure of the CO<sub>2</sub> gas flowing through the CO<sub>2</sub> gas flow path **23** is controlled. Because the differential pressure between the pressure of the cathode solution and the pressure of the CO<sub>2</sub> gas affects the production amount and the proportion of each product, controlling the differential pressure based on a detection result of the reduction product makes it possible to adjust the production amount and the proportion of each product in a desired state.

**[0042]** When the differential pressure between the pressure of the cathode solution and the pressure of the CO<sub>2</sub> gas is too large, there is a possibility that the CO<sub>2</sub> gas permeates the cathode solution flow path **21** or the cathode solution permeates the CO<sub>2</sub> gas flow path **23**. Both of these become a factor of impairing the reduction reaction of CO<sub>2</sub> in the cathode **22**. Therefore, an absolute value of the differential pressure between the pressure of the cathode solution and the pressure of the CO<sub>2</sub> gas is preferably set to 100 kPa or less. Further, when the absolute value of the differential pressure between the pressure of the cathode solution and the pressure of the CO<sub>2</sub> gas is too small, a function of adjusting the production amount and the proportion of each product decreases, and therefore the absolute value of the differential pressure is preferably 0.1 kPa or more. The absolute value of the differential pressure is more preferably 0.1 kPa or more to 10 kPa or less. Specific control contents of the differential pressure between the pressure of the cathode solution and the pressure of the CO<sub>2</sub> gas will be described later.

**[0043]** Next, an operation of the carbon dioxide electrolytic device **1** of the embodiment will be described. Here, a case of producing carbon monoxide (CO) as the carbon compound is mainly described, but the carbon compound as the reduction product of carbon dioxide is not limited to carbon monoxide. The carbon compound may be methane (CH<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), methanol (CH<sub>3</sub>OH), ethanol (C<sub>2</sub>H<sub>5</sub>OH), ethylene glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>), or the like as described above, and further carbon monoxide which is the reduction product may be further reduced to produce the organic compounds as described above. Further, as a reaction process by the electrolysis cell **2**, a case of mainly producing hydrogen ions (H<sup>+</sup>) and a case of mainly producing hydroxide ions (OH<sup>-</sup>) are considered, but it is not limited to either of these reaction processes.

**[0044]** First, the reaction process in a case of mainly oxidizing water (H<sub>2</sub>O) to produce hydrogen ions (H<sup>+</sup>) is described. When an electric current is supplied from the power supply **40** between the anode **11** and the cathode **22**, the oxidation reaction of water (H<sub>2</sub>O) occurs in the anode **11** in contact with the anode solution. Specifically, as indicated by the following (1) formula, H<sub>2</sub>O contained in the anode solution is oxidized and oxygen (O<sub>2</sub>) and hydrogen ions (H<sup>+</sup>) are produced.



**[0045]** H<sup>+</sup> produced in the anode **11** moves in the anode solution existing in the anode **11**, the separator **30**, and the cathode solution in the cathode solution flow path **21** and reaches the vicinity of the cathode **22**. The reduction reaction of carbon dioxide (CO<sub>2</sub>) occurs by electrons (e<sup>-</sup>) based on the electric current which is supplied from the power supply **40** to the cathode **22** and H<sup>+</sup> which moves to the vicinity of the cathode **22**. Specifically, as indicated by the following (2) formula, CO<sub>2</sub> supplied from the CO<sub>2</sub> gas flow path **23** to the cathode **22** is reduced and CO is produced.



**[0046]** Next, the reaction process in a case of mainly reducing carbon dioxide (CO<sub>2</sub>) to produce hydroxide ions (OH<sup>-</sup>) is described. When an electric current is supplied from the power supply **40** between the anode **11** and the cathode **22**, in the vicinity of the cathode **22**, as indicated by the following (3) formula, water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>) are reduced and carbon monoxide (CO) and hydroxide ions (OH<sup>-</sup>) are produced. The hydroxide ions (OH<sup>-</sup>) diffuse in the vicinity of the anode **11**, and as indicated by the following (4) formula, the hydroxide ions (OH<sup>-</sup>) are oxidized and oxygen (O<sub>2</sub>) is produced.



**[0047]** In the above-described reaction processes in the cathode **22**, the reduction reaction of CO<sub>2</sub> is considered to occur in the vicinity of the boundary between the gas diffusion layer **22a** and the cathode catalyst layer **22b** as described above. At this time, when the pressure of the cathode solution flowing through the cathode solution flow path **21** is larger than the pressure of the CO<sub>2</sub> gas flowing through the CO<sub>2</sub> gas flow path **23**, production of H<sub>2</sub> by the reduction reaction of H<sub>2</sub>O in the cathode solution sometimes has superiority to production of CO by the reduction reaction of CO<sub>2</sub>. In the above case, the production amount and the proportion of H<sub>2</sub> in the reduction product increase and the production amount and the proportion of intended CO decrease. In such a case, the differential pressure is adjusted by the data collection control unit **502** functioning as a differential pressure control unit so that the pressure of the CO<sub>2</sub> gas is larger than the pressure of the cathode solution, thereby making the reduction reaction of CO<sub>2</sub> preferentially occur in the vicinity of the boundary between the gas diffusion layer **22a** and the cathode catalyst layer **22b**. This makes it possible to increase the production amount and the production proportion of CO by the reduction reaction of CO<sub>2</sub>. The specific differential pressure is preferably 0.1 kPa or more to 100 kPa or less, and more preferably 0.1 kPa or more to 10 kPa or less as described above.

**[0048]** As described above, the differential pressure between the pressure of the cathode solution flowing through the cathode solution flow path **21** and the pressure of the CO<sub>2</sub> gas flowing through the CO<sub>2</sub> gas flow path **23** is preferably adjusted so that the pressure of the CO<sub>2</sub> gas is larger than the pressure of the cathode solution. However, this is not necessarily restrictive. For example, when the gas diffusion layer **22a** has high water repellency and the cathode solution does not easily enter the gas diffusion layer **22a**, or when the CO<sub>2</sub> gas easily leaks to the cathode catalyst layer **22b** side, an adjustment may be made so that the pressure of the cathode solution is larger than the pressure of the CO<sub>2</sub> gas. In both cases, since the differential pressure between the pressure of the cathode solution and the pressure of the CO<sub>2</sub> gas affects the production amount and the proportion of each product, the differential pressure is adjusted so that they each become a desired value, based on the production amount and the proportion of each product detected in the reduction performance detection unit **501**. This makes it possible to obtain the reduction product having desired production amount and proportion.

**[0049]** Further, in both of the above-described reaction process in which hydrogen ions (H<sup>+</sup>) are mainly produced

and reaction process in which hydroxide ions ( $\text{OH}^-$ ) are mainly produced, oxygen ( $\text{O}_2$ ) is produced in the anode **11**. At this time, for example, in a cell structure in which a separator is sandwiched by a cathode solution flow path and an anode solution flow path, air bubbles of oxygen ( $\text{O}_2$ ) gas which occur in the anode **11** stay in the anode solution flow path, and cell resistance between the anode and the separator (ion exchange membrane or the like) increases, and thereby a voltage variation of the anode is considered to become large. In contrast to this, in the electrolysis cell **2** of the embodiment, the anode solution flow path **12** is not disposed between the anode **11** and the separator **30**, and the anode **11** and the separator **30** are brought in close contact with each other, and therefore oxygen gas which occurs in the anode **11** is discharged to the anode solution flow path **12** together with the anode solution. Therefore, it is possible to prevent the oxygen gas from staying between the anode **11** and the separator **30**. Accordingly, it becomes possible to suppress a variation in a cell voltage due to the voltage variation of the anode.

[0050] Moreover, in the electrolysis cell **2** of the embodiment, providing the lands **15** and the lands **29** along the anode solution flow path **12** and the  $\text{CO}_2$  gas flow path **23** makes it possible to increase a contact area between the anode **11** and the first flow path plate **14** constituting the anode solution flow path **12** and a contact area between the cathode **22** and the third flow path plate **28** constituting the  $\text{CO}_2$  gas flow path **23**. Further, providing the land **26** in the cathode solution flow path **21** makes it possible to increase a contact area between the cathode **22** and the second flow path plate **25** constituting the cathode solution flow path **21**. These make electrical continuity between the anode current collector **13** and the cathode current collector **24** good while enhancing mechanical retentivity of the electrolysis cell **2**, and make it possible to improve reduction reaction efficiency of  $\text{CO}_2$ , or the like.

#### EXAMPLE

[0051] Next, an example and its evaluation result will be described.

##### Example 1

[0052] An electrolytic device illustrated in FIG. 1 and FIG. 2 was fabricated as follows, and electrolysis performance of carbon dioxide was examined. First, on carbon paper on which a porous layer was provided, a cathode to which gold nanoparticle-supported carbon particles were applied was produced by the following process. A coating solution in which the gold nanoparticle-supported carbon particles and pure water, a Nafion solution, and ethylene glycol were mixed was produced. An average particle diameter of the gold nanoparticle was 8.7 nm, and a supported amount thereof was 18.9 mass %. An air brush was filled with this coating solution, spray coating was performed using Ar gas on the carbon paper on which the porous layer was provided. Flowing water washing was performed by pure water for 30 minutes after the coating, and thereafter organic matter such as ethylene glycol was removed by oxidation through immersing in a hydrogen peroxide solution. This was cut into a size of 2×2 cm to be set as the cathode. Note that a coating amount of Au was estimated at about 0.2 mg/cm<sup>2</sup> from a mixing amount of the gold nanoparticles and the carbon particles in the coating solution.

[0053] For an anode, an electrode in which  $\text{IrO}_2$  nanoparticles which became a catalyst were applied to Ti mesh was used. As the anode, the one in which  $\text{IrO}_2/\text{Ti}$  mesh was cut into 2×2 cm was used.

[0054] The electrolysis cell **2** was produced by being stacked in order of the cathode current collector **24**, the  $\text{CO}_2$  gas flow path **23** (the third flow path plate **28**), the cathode **22**, the cathode solution flow path **21** (the second flow path plate **25**), the separator **30**, the anode **11**, the anode solution flow path **12** (the first flow path plate **14**), and the anode current collector **13** from the top, being sandwiched by the support plates not illustrated, and further being tightened by the bolts, as illustrated in FIG. 2. For the separator **30**, an anion exchange membrane (brand name: Selemion, manufactured by ASAHI GLASS CO., LTD.) was used. The  $\text{IrO}_2/\text{Ti}$  mesh of the anode **11** was brought in close contact with the anion exchange membrane. A thickness of the cathode solution flow path **21** was set to 1 mm. Note that an evaluation temperature was set to room temperature.

[0055] The electrolytic device illustrated in FIG. 1 was operated under the following condition.  $\text{CO}_2$  gas was supplied to the  $\text{CO}_2$  gas flow path of the electrolysis cell at 20 sccm, an aqueous potassium hydroxide solution (concentration 1 M KOH) was introduced to the cathode solution flow path at a flow rate of 5 mL/min, and the aqueous potassium hydroxide solution (concentration 1 M KOH) was introduced to the anode solution flow path at a flow rate of 20 mL/min. A differential pressure between the  $\text{CO}_2$  gas and the cathode solution was controlled so that a pressure of the  $\text{CO}_2$  gas was 2.5 kPa larger than a pressure of the cathode solution, so as to adjust a proportion of a reduction product. Next, a 600 mA constant current (constant current density 150 mA/cm<sup>2</sup>) was passed between the anode and the cathode using the power supply, an electrolytic reaction of  $\text{CO}_2$  was performed, and a cell voltage, an anode potential, and a cathode potential at that time were measured. Note that a Hg/HgO reference electrode (+0.098 V vs. SHE) was used for potential measurement, and pH was set to 13.65 to calculate an overvoltage. Part of gas outputted from the  $\text{CO}_2$  gas flow path was collected, and production amounts of CO gas to be produced by a reduction reaction of  $\text{CO}_2$  and  $\text{H}_2$  gas to be produced by a reduction reaction of water were analyzed by a gas chromatograph. From these gas production amounts, a partial current density and Faraday's efficiency which is a ratio between the entire current density and the partial current density of CO or  $\text{H}_2$  were calculated.

[0056] FIG. 10 illustrates time changes in the cell voltage, the anode potential, and the cathode potential. Table 1 presents an average value of the cell voltage, an anode overvoltage, and a cathode overvoltage between 300 seconds and 570 seconds when gas collection is performed, and the Faraday's efficiency, the partial current density, and electrolysis efficiency of CO and  $\text{H}_2$ . As presented in Table 1, good electrolysis performance having high selectivity of CO, such as 2.76 V in the cell voltage, 83% in the Faraday's efficiency of CO, and 40% in the electrolysis efficiency of CO, was obtained.

TABLE 1

EXAMPLE 1	
CELL VOLTAGE [V]*	2.76
ANODE OVERVOLTAGE [V]*	0.53

TABLE 1-continued

EXAMPLE 1	
CATHODE OVERVOLTAGE [V]*	0.39
CO FARADAY'S EFFICIENCY [%]	83
H <sub>2</sub> FARADAY'S EFFICIENCY [%]	13
CO PARTIAL CURRENT DENSITY [mA/cm <sup>2</sup> ]	125
H <sub>2</sub> PARTIAL CURRENT DENSITY [mA/cm <sup>2</sup> ]	15.8
ELECTROLYSIS EFFICIENCY OF CO [%]	40
ELECTROLYSIS EFFICIENCY OF H <sub>2</sub> [%]	5.6
ELECTROLYSIS EFFICIENCY OF CO AND H <sub>2</sub> [%]	46

\*AVERAGE VALUE OF 300 s TO 570 s.

## Reference Example 1

**[0057]** An electrolytic reaction of CO<sub>2</sub> was performed similarly to Example 1 except that the differential pressure between the CO<sub>2</sub> gas and the cathode solution was changed, and performance was evaluated. The differential pressure between the CO<sub>2</sub> gas and the cathode solution was controlled at -0.6 kPa under a condition in which the pressure of the cathode solution was larger. Table 2 presents each of performance values found similarly to Example 1. As presented in Table 2, low selectivity and low electrolysis efficiency of CO as compared with Example 1, such as 3.12 V in the cell voltage, 21% in the Faraday's efficiency of CO, and 9% in the electrolysis efficiency of CO were confirmed. From these results, it was confirmed that improvement in the selectivity and the electrolysis efficiency of CO was achieved by controlling the differential pressure between the CO<sub>2</sub> gas and the cathode solution.

TABLE 2

REFERENCE EXAMPLE 1	
CELL VOLTAGE [V]*	3.12
ANODE OVERVOLTAGE [V]*	0.51
CATHODE OVERVOLTAGE [V]*	0.43
CO FARADAY'S EFFICIENCY [%]	21
H <sub>2</sub> FARADAY'S EFFICIENCY [%]	25
CO PARTIAL CURRENT DENSITY [mA/cm <sup>2</sup> ]	31
H <sub>2</sub> PARTIAL CURRENT DENSITY [mA/cm <sup>2</sup> ]	31.2
ELECTROLYSIS EFFICIENCY OF CO [%]	9
ELECTROLYSIS EFFICIENCY OF H <sub>2</sub> [%]	9.9
ELECTROLYSIS EFFICIENCY OF CO AND H <sub>2</sub> [%]	19

\*AVERAGE VALUE OF 300 s TO 570 s.

**[0058]** Note that configurations of the above-described embodiments may be each applied in combination, and further may be partially substituted. Herein, while certain embodiments of the invention have been described, these embodiments have been presented by way of example only, and are not intended to limit the scope of the inventions. Indeed, the novel embodiments described herein may be embodied in a variety of other forms; furthermore, various omissions, substitutions, and changes in the form of the embodiments described herein may be made without departing from the spirit of the inventions. The accompanying claims and their equivalents are intended to cover such forms or modifications as would fall within the scope and spirit of the invention.

What is claimed is:

1. A carbon dioxide electrolytic device comprising:

a cathode part including a cathode to reduce carbon dioxide and thus produce a carbon compound, a cath-

ode solution flow path to supply a cathode solution to the cathode, and a gas flow path to supply carbon dioxide to the cathode;

an anode part including an anode to oxidize water or hydroxide ions and thus produce oxygen and an anode solution flow path to supply an anode solution to the anode;

a separator to separate the anode part and the cathode part;

a power supply to pass an electric current between the anode and the cathode;

a first pressure control unit to control a pressure of the cathode solution flowing in the cathode solution flow path;

a second pressure control unit to control a pressure of the carbon dioxide flowing in the gas flow path;

a detection unit to detect a production amount of the carbon compound produced by a reduction reaction in the cathode part; and

a differential pressure control unit to control a differential pressure between a pressure of the cathode solution and a pressure of the carbon dioxide so as to adjust the production amount of the carbon compound detected in the detection unit.

2. The device according to claim 1, wherein the differential pressure control unit controls the first and second pressure control units so that an absolute value of the differential pressure between the pressure of the cathode solution and the pressure of the carbon dioxide is 0.1 kPa or more to 100 kPa or less.

3. The device according to claim 1, wherein the differential pressure control unit controls the first and second pressure control units so that the pressure of the carbon dioxide is larger than the pressure of the cathode solution.

4. The device according to claim 1,

wherein the anode has a first surface in contact with the separator and a second surface facing the anode solution flow path so that the anode solution is in contact with the anode, and

wherein the cathode has a first surface facing the cathode solution flow path and a second surface facing the gas flow path, and the cathode solution flow path is disposed between the separator and the cathode so that the cathode solution is in contact with the separator and the cathode.

5. The device according to claim 4, wherein the cathode has a gas diffusion layer disposed on the second surface side and a catalyst layer disposed on the first surface side and constituted of a cathode catalyst provided on the gas diffusion layer.

6. The device according to claim 5, wherein the cathode catalyst contains at least one metal selected from the group consisting of Au, Ag, Cu, Pt, Pd, Ni, Co, Fe, Mn, Ti, Cd, Zn, In, Ga, Pb, and Sn, and has at least one selected from the group consisting of nanoparticles of the metal, a nanostructure of the metal, nanowires of the metal, and a composite body in which the nanoparticles are supported by carbon particles, carbon nanotubes, or graphene.

7. The device according to claim 4,

wherein the anode includes a base material having at least one selected from the group consisting of a mesh material, a punching material, a porous body, and a metal fiber sintered body, and



wherein the anode has the base material constituted of an anode catalyst or a catalyst layer constituted of an anode catalyst provided on a surface of the base material.

**8.** The device according to claim 7, wherein the base material is constituted of a metal material containing at least one selected from the group consisting of Ti, Ni, and Fe, and the anode catalyst is constituted of a metal material containing at least one metal selected from the group consisting of Ni, Fe, Co, Mn, La, Ru, Li, Ir, In, Sn, and Ti, or an oxide material containing the metal.

**9.** The device according to claim 1, wherein the anode solution and the cathode solution contain at least one ion selected from the group consisting of a hydroxide ion, a hydrogen ion, a potassium ion, a sodium ion, a lithium ion, a chloride ion, a bromide ion, an iodide ion, a nitrate ion, a sulfate ion, a phosphate ion, a borate ion, and a hydrogen carbon ion.

**10.** The device according to claim 1, wherein the carbon compound to be produced by a reduction reaction of the carbon dioxide contains at least one selected from the group consisting of carbon monoxide, methane, ethane, ethylene, methanol, ethanol, and ethylene glycol.

\* \* \* \* \*