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(54) CATHODE ELECTRODE, AND COMPOSITE BODY OF CATHODE ELECTRODE AND BASE MATERIAL

(57) The present invention provides a cathode electrode in which selectivity of hydrogen decreases and selectivity of a carbon dioxide reduction product increases in a catalytic reaction producing carbon monoxide, an olefinic hydrocarbon such as ethylene, and an alcohol such as ethanol by a reduction reaction of carbon dioxide.

A cathode electrode that electrically reduces carbon dioxide, including: a first layer containing cuprous oxide, copper, and at least one additional metal element selected from the group consisting of silver, gold, zinc, cadmium, and tin; and a second layer formed on the first layer and containing a constituent element composed of at least one metal element selected from the group consisting of copper, silver, gold, zinc, cadmium, and tin.

EP 4 464 822 A1

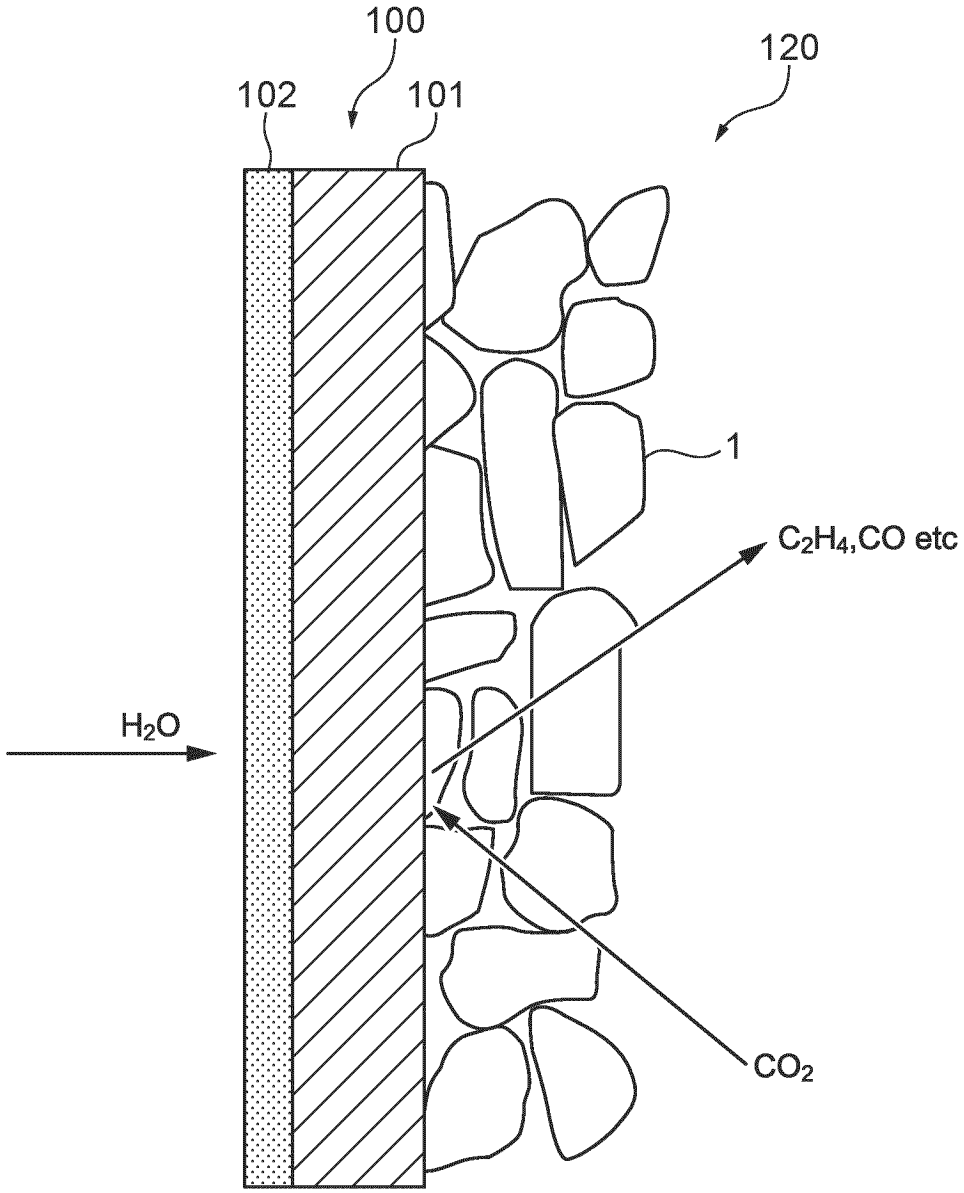


FIG.1

Description

Technical Field

[0001] The present invention relates to a cathode electrode that can electrically reduce carbon dioxide to convert carbon dioxide into carbon monoxide, an olefinic hydrocarbon such as ethylene, and/or an alcohol, and a composite of a cathode electrode and a substrate.

Background Art

[0002] In recent years, adverse effects due to the global warming have diversely changed the global environment, and various problematic phenomena are occurring. One of the causes is considered to be a rise in concentration of greenhouse gasses in the atmosphere, specifically carbon dioxide, which mainly accounts for the greenhouse gasses. To lower the concentration of carbon dioxide in the atmosphere, not only increasing an amount of photosynthesis by new afforestation on the ground and marine algae but also actively absorbing and recovering carbon dioxide in the atmosphere has been investigated. Furthermore, not only absorbing and recovering carbon dioxide but also utilizing carbon derived from carbon dioxide as a raw material of organic compounds are desirable.

[0003] Specifically, it has been investigated to reduce carbon dioxide and convert it into, for example, ethylene, ethanol, carbon monoxide, methane, methanol, formic acid, and the like to be utilized for synthesizing organic compounds. Among them, specifically ethylene and ethanol, which are C2 compounds, are significantly useful as derivatives with synthesizing various organic compounds, and have higher utility value than C1 compounds such as carbon monoxide and methane.

[0004] In recent years, for the reduction reaction of carbon dioxide as above, catalysts such as photocatalysts and electrode catalysts have been commonly used, and development of a catalyst having more excellent performance is required. In a catalyst used for the reduction reaction of carbon dioxide, not only reaction efficiency but also selectivity to a specific reaction are required, and selecting a material is important from such a viewpoint (Non-Patent Literature 1). For example, from the viewpoint of efficient reductive production of carbon monoxide to increase a rate of carbon monoxide in the reduced substances, gold, silver, and zinc are used as the catalyst material. From the viewpoint of efficient reductive production of a hydrocarbon such as methane, ethane, and ethylene, copper is used as the catalyst material. Among them, copper attracts attention as an electrode catalyst for a cathode reduction of carbon dioxide because it can produce a C2 compound such as ethylene.

[0005] Proposed as the electrode catalyst for the cathode reduction of carbon dioxide using copper is, for example, a cathode electrode for reducing carbon dioxide that inhibits diffusion of the metal element between a catalyst layer and a substrate and inhibits a side reaction of the metal and that inhibits deterioration of catalytic efficiency by forming a diffusion inhibiting layer composed of an organic material on the substrate and by forming the catalyst layer mainly composed of a metal cluster thereon (Patent Literature 1). Meanwhile, evaluated in Example of Patent Literature 1 is a Faraday efficiency of each product such as ethylene in the reduction reaction of carbon dioxide. In Patent Literature 1, stably sustaining the catalytic reaction producing the organic compounds such as ethylene over a long term is not verified.

[0006] To practically use the production of the organic compounds such as ethylene with the reduction reaction of carbon dioxide in the industry, the catalytic reaction producing the organic compounds such as ethylene is required to be stably sustained in a term as long as several hundred hours or longer. The cathode electrode for reducing carbon dioxide of Patent Literature 1 has room for improvement from the viewpoint of stably sustaining the catalytic reaction producing the organic compounds such as ethylene over a long term.

[0007] To obtain excellent synthesis efficiency of the organic compound with the cathode electrode for reducing carbon dioxide, it is required for reducing carbon dioxide that a selectivity of hydrogen is reduced by dominance of the reduction reaction of carbon dioxide over production of hydrogen caused by a side reaction (decomposition reaction of water), and that a selectivity of the carbon dioxide reduction product be improved. However, In Patent Literature 1, reduction in the selectivity of hydrogen and improvement of the selectivity of the carbon dioxide reduction product in the reduction of carbon dioxide are not verified. The cathode electrode for reducing carbon dioxide of Patent Literature 1 has room for improvement from the viewpoint of reducing the selectivity of hydrogen and improving the selectivity of the carbon dioxide reduction product.

Document List

Patent Literature

[0008] Patent Literature 1: Japanese Patent Application Laid-Open No. 2018-168410

Non-Patent Literature

[0009] Non-Patent Literature 1: Y Hori "Electrochemical reduction of CO at a Copper Electrode." J. Phys. Chem. B. 101(36). 7075-7081 (1997)

Summary of Invention

Technical Problem

[0010] Considering the above situation, it is an object of the present invention to provide a cathode electrode that reduces the selectivity of hydrogen and improves the selectivity of the carbon dioxide reduction product in a catalytic reaction producing carbon monoxide, an olefinic hydrocarbon such as ethylene, and an alcohol such as ethanol by the reduction reaction of carbon dioxide, and a composite of the cathode electrode and a substrate.

Solution to Problem

[0011] The spirits of constitutions of the present invention are as follows.

[1] A cathode electrode that electrically reduces carbon dioxide, comprising:

a first layer containing cuprous oxide, copper, and at least one additional metal element selected from the group consisting of silver, gold, zinc, cadmium, and tin; and
a second layer formed on at least a part of a region on the first layer and containing a constituent element composed of at least one metal element selected from the group consisting of copper, silver, gold, zinc, cadmium, and tin.

[2] A cathode electrode that electrically reduces carbon dioxide, comprising:

a first layer containing cuprous oxide and at least one additional metal element selected from the group consisting of silver, gold, zinc, cadmium, and tin; and
a second layer formed on at least a part of a region on the first layer and containing a constituent element composed of at least one metal element selected from the group consisting of copper, silver, gold, zinc, cadmium, and tin.

[3] The cathode electrode according to [2], wherein a part of cuprous oxide in the first layer is reduced to copper by a reduction treatment.
[4] The cathode electrode according to [1] or [2], wherein the second layer is a protective layer for the first layer.
[5] The cathode electrode according to any one of [1] to [4], wherein the constituent element of the second layer contains a silver element.
[6] The cathode electrode according to [5], wherein the silver element as the constituent element is in a state of simple substance of silver or an oxide of silver.
[7] The cathode electrode according to any one of [1] to [6], wherein the additional metal element of the first layer contains a zinc element.
[8] The cathode electrode according to any one of [1] to [7], wherein an average thickness of the second layer is 10 nm or more and 200 nm or less.
[9] The cathode electrode according to any one of [1] to [8], wherein a value of the number of moles of a copper element / the number of moles of an oxygen element in the first layer is 1.5 or more and 5.1 or less.
[10] The cathode electrode according to any one of [1] to [9], wherein the first layer has a porous structure.
[11] A composite of a cathode electrode and a substrate, comprising: a substrate having a porous structure; and the cathode electrode according to any one of [1] to [10] in which a side of the first layer is disposed on the substrate.
[12] The composite according to [11], wherein the substrate is porous carbon.
[13] An electrolytic reduction apparatus that electrically reduces carbon dioxide to carbon monoxide, an olefinic hydrocarbon, and/or an alcohol, comprising the cathode electrode according to any one of [1] to [10].
[14] An electrolytic reduction apparatus that electrically reduces carbon dioxide to carbon monoxide, an olefinic hydrocarbon, and/or an alcohol, comprising the composite according to [11] or [12].
[15] A method of manufacturing a composite of a cathode electrode and a substrate, comprising:

a step of providing a substrate having a porous structure;

a first coelectrodeposition layer forming step of coelectrodepositing cuprous oxide and at least one additional metal element selected from the group consisting of silver, gold, zinc, cadmium, and tin on the substrate to form a first coelectrodeposition layer that is a first layer; and
a second layer forming step of forming a film with a constituent element composed of at least one metal element selected from the group consisting of copper, silver, gold, zinc, cadmium, and tin to form a second layer on at least a part of a region on the first coelectrodeposition layer.

[16] The manufacturing method according to [15], further comprising a partial reduction step of partially reducing the first coelectrodeposition layer and the second layer after the second layer forming step.
[17] The manufacturing method according to [15] or [16], wherein the substrate is porous carbon.

[0012] The term "value of the number of moles of a copper element / the number of moles of an oxygen element in the first layer" in the description "value of the number of moles of a copper element / the number of moles of an oxygen element in the first layer is 1.5 or more and 5.1 or less" means a value of the number of moles of a copper element / the number of moles of an oxygen element obtained from a spectrum measured by energy-dispersive X-ray spectrometry (EDS) of a surface of the first layer by using a desktop scanning electron microscope Phenom G6 ProX under measurement under conditions of an acceleration voltage of 15 kV and a magnification of 5000 to 10000.

Effects of Invention

[0013] In an aspect of the cathode electrode of the present invention, on a first layer containing cuprous oxide, copper, and at least one additional metal element selected from the group consisting of silver, gold, zinc, cadmium, and tin, a second layer containing a constituent element composed of at least one metal element selected from the group consisting of copper, silver, gold, zinc, cadmium, and tin is formed. The first layer functions as a catalyst layer to reduce carbon dioxide. The second layer functions as a protective layer for the first layer and as a layer having a catalytic ability to reduce carbon dioxide. Accordingly, in the aspect of the cathode electrode of the present invention, the layers having the catalytic activity have a stacked structure. In the aspect of the cathode electrode of the present invention, it is considered that active sites of the carbon dioxide reduction increase and an amount of water entering the first layer is regulated within an appropriate range by the presence of the second layer, and thereby a ratio between water and carbon dioxide in a site of the reduction reaction of carbon dioxide is regulated within an appropriate range in the cathode electrode. Therefore, in the aspect of the cathode electrode of the present invention, it is considered that the reduction reaction of carbon dioxide becomes dominant over the hydrogen production reaction, which is a side reaction, the selectivity of the carbon dioxide reduction product increases, and the hydrogen selectivity decreases. It is considered that, by the presence of the second layer, reduction from cuprous oxide to copper in a deep portion of the first layer (that is, in the first layer, a portion on the opposite side to the second layer) is particularly inhibited, and the value of the number of moles of the copper element / the number of moles of the oxygen element in the first layer is sustained within an appropriate range for a long time, the properties of ability to stably sustain the high efficiency of the catalytic reaction producing the olefinic hydrocarbon such as ethylene and the alcohol such as ethanol with the reduction reaction of carbon dioxide over a long term (hereinafter, which may be referred to as "stability") tends to increase while improving the selectivity of the carbon dioxide reduction product.
[0014] In the aspect of the cathode electrode of the present invention, a particularly remarkable effect is exhibited in an embodiment in which gaseous carbon dioxide is supplied from the opposite side to the second layer across the first layer to the cathode electrode, and a deep portion in the first layer can be a main reaction site of the reduction reaction of carbon dioxide.
[0015] Therefore, according to the aspect of the cathode electrode of the present invention, by containing: the first layer containing cuprous oxide, copper, and at least one additional metal element selected from the group consisting of silver, gold, zinc, cadmium, and tin; and the second layer formed on the first layer and containing a constituent element composed of at least one metal element selected from the group consisting of copper, silver, gold, zinc, cadmium, and tin, or by containing: the first layer containing cuprous oxide and at least one additional metal element selected from the group consisting of silver, gold, zinc, cadmium, and tin; and the second layer formed on the first layer and containing a constituent element composed of at least one metal element selected from the group consisting of copper, silver, gold, zinc, cadmium, and tin, the selectivity of hydrogen decreases and the selectivity of the carbon dioxide reduction product increases in the catalytic reaction producing carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol with the reduction reaction of carbon dioxide.
[0016] According to the aspect of the cathode electrode of the present invention, by containing a silver element in the constituent element of the second layer, the reduction from carbon dioxide to carbon monoxide in the second layer is more enhanced, hydrogen production is inhibited and the hydrogen selectivity more certainly decreases, a C-C bond reaction with carbon monoxide reduced in the second layer is more enhanced with the catalytic action in the first layer to consequently produce the olefinic hydrocarbon such as ethylene and the alcohol such as ethanol, and thereby the

selectivity of the carbon dioxide reduction product more certainly increases.

[0017] According to the aspect of the cathode electrode of the present invention, by the additional metal element in the first layer containing a zinc element, the selectivity of hydrogen more certainly decreases and the selectivity of the carbon dioxide reduction product more certainly increases in the catalytic reaction producing carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol with the reduction reaction of carbon dioxide.

[0018] According to the aspect of the cathode electrode of the present invention, by the average thickness of the second layer of 10 nm or more and 200 nm or less, active sites of the carbon dioxide reduction certainly increase and an amount of water entering the first layer is certainly regulated within an appropriate range, and thereby the selectivity of the carbon dioxide reduction product certainly increases and the hydrogen selectivity certainly decreases.

[0019] According to the aspect of the cathode electrode of the present invention, by the value of the number of moles of a copper element / the number of moles of an oxygen element in the first layer being within a range of 1.5 or more and 5.1 or less, the selectivity of the carbon dioxide reduction product certainly increases and the hydrogen selectivity certainly decreases, and the catalytic reaction producing carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol with the reduction reaction of carbon dioxide can be stably sustained over a further longer term.

[0020] According to the aspect of the cathode electrode of the present invention, by the first layer having the porous structure, the catalytic reaction producing carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol with the reduction reaction of carbon dioxide can be further stably sustained over a long term, and the selectivity of the carbon dioxide reduction product certainly increases and the hydrogen selectivity certainly decreases.

[0021] According to the aspect of the composite of the cathode electrode and the substrate of the present invention, by comprising the cathode electrode of the present invention, the selectivity of hydrogen decreases and the selectivity of the carbon dioxide reduction product increases in the catalytic reaction producing carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol with the reduction reaction of carbon dioxide.

[0022] According to the aspect of the composite of the cathode electrode and the substrate of the present invention, by the substrate, which is porous carbon, gaseous carbon dioxide can be smoothly contacted with the first layer, and therefore, even with the gaseous carbon dioxide, the catalytic reaction producing carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol with the reduction reaction of carbon dioxide can be further stably sustained over a long term, and the selectivity of the carbon dioxide reduction product certainly increases and the hydrogen selectivity certainly decreases.

Brief Description of Drawings

[0023]

[FIG. 1] An explanatory diagram illustrating an outline of a cross section of the composite of the cathode electrode and the substrate of the present invention.

[FIG. 2] An explanatory diagram of the electropolishing treatment step in the method of manufacturing the composite of the cathode electrode and the substrate.

[FIG. 3] An explanatory diagram of the coelectrodeposition layer forming step in the method of manufacturing the composite of the cathode electrode and the substrate.

[FIG. 4] An explanatory diagram of the partial reduction step in the method of manufacturing the composite of the cathode electrode and the substrate.

[FIG. 5] An explanatory diagram illustrating an outline of the electrolytic reduction apparatus having the cathode electrode of the present invention.

Description of Embodiments

[Cathode Electrode]

[0024] The cathode electrode of the present invention will be described below. A first cathode electrode of the present invention, which is a cathode electrode that electrically reduces carbon dioxide, comprises: a first layer containing cuprous oxide (Cu_2O), copper (Cu), and at least one additional metal element (M1) selected from the group consisting of silver (Ag), gold (Au), zinc (Zn), cadmium (Cd), and tin (Sn); and a second layer formed on the first layer and containing a constituent element (M2) composed of at least one metal element selected from the group consisting of copper (Cu), silver (Ag), gold (Au), zinc (Zn), cadmium (Cd), and tin (Sn). The above first layer of the cathode electrode of the present invention contains cuprous oxide (Cu_2O), copper (Cu), and the additional metal element (M1) as essential components.

[0025] In the first cathode electrode of the present invention, by the first layer containing cuprous oxide (CuzO), copper (Cu), and at least one additional metal element (M1) selected from the group consisting of silver (Ag), gold (Au), zinc (Zn), cadmium (Cd), and tin (Sn) as the essential components, the first layer becomes a site of the catalytic reaction producing

carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol with the reduction reaction of carbon dioxide, and therefore the first layer functions as a catalyst layer of the first cathode electrode.

[0026] In the first cathode electrode, the second layer covers at least a part of a region of a surface of the first layer, and therefore the second layer has a function as a protective layer for the first layer. In the first cathode electrode, the second layer is formed continuously to the first layer, and directly contacted on the surface of the first layer. The second layer contains the constituent element (M2) having reduction ability composed of at least one metal element selected from the group consisting of copper (Cu), silver (Ag), gold (Au), zinc (Zn), cadmium (Cd), and tin (Sn), and therefore the second layer also functions as a layer having a catalytic ability to reduce carbon dioxide. In the first cathode electrode, there is a boundary between the first layer and the second layer, and thus the first layer and the second layer can be distinguished by microscope observation or the like.

[0027] In the first cathode electrode, the second layer having the catalytic ability to reduce carbon dioxide is provided in addition to the first layer functioning as the catalyst layer, and active sites for the carbon dioxide reduction consequently increase. In the first cathode electrode, it is considered that, by providing the second layer also having the function as the protective layer for the first layer, an amount of water entering the first layer is regulated within an appropriate range and a ratio between water and carbon dioxide in the site of the reduction reaction of carbon oxide is regulated within an appropriate range in the first cathode electrode. As side reactions of the reduction reaction of carbon dioxide, a decomposition reaction of water is mentioned, but in the first cathode electrode, the ratio between water and carbon dioxide in the site of the reduction reaction of carbon oxide is regulated within an appropriate range, and therefore it is considered that the reduction reaction of carbon dioxide becomes dominant over the hydrogen production reaction (that is, the decomposition reaction of water), which is the side reaction, the selectivity of the carbon dioxide reduction product increases, and the hydrogen selectivity decreases. It is considered that, by the second layer functioning as the protective layer for the first layer, reduction from cuprous oxide to copper in the first layer is inhibited and the value of the number of moles of the copper element / the number of moles of the oxygen element in the first layer is regulated within an appropriate range for a long time, and thereby the properties of ability to stably sustain the high efficiency of the catalytic reaction producing the olefinic hydrocarbon and the alcohol over a long term tends to increase.

[0028] Therefore, according to the aspect of the first cathode electrode, by containing: the first layer containing cuprous oxide, copper, and at least one additional metal element selected from the group consisting of silver, gold, zinc, cadmium, and tin; and the second layer formed on the first layer and containing a constituent element composed of at least one metal element selected from the group consisting of copper, silver, gold, zinc, cadmium, and tin, the selectivity of hydrogen decreases and the selectivity of the carbon dioxide reduction product increases in the above catalytic reaction.

[0029] A second cathode electrode of the present invention, which is a cathode electrode that electrically reduces carbon dioxide, comprises: a first layer containing cuprous oxide (Cu_2O) and at least one additional metal element (M1) selected from the group consisting of silver (Ag), gold (Au), zinc (Zn), cadmium (Cd), and tin (Sn); and a second layer formed on the first layer and containing a constituent element (M2) composed of at least one metal element selected from the group consisting of copper (Cu), silver (Ag), gold (Au), zinc (Zn), cadmium (Cd), and tin (Sn). In the first layer of the second cathode electrode, a part of cuprous oxide (Cu_2O) is reduced to copper (Cu). That is, a part of cuprous oxide (CuzO) in the first layer is reduced to copper (Cu) by a reduction treatment. The first layer of the second cathode electrode of the present invention contains cuprous oxide (CuzO) and the above additional metal element (M1) as essential components. The first layer of the second cathode electrode of the present invention is subjected to the reduction treatment, and cuprous oxide (CuzO) for reduction is reduced to copper (Cu) to form the cathode electrode containing cuprous oxide (CuzO), copper (Cu), and at least one additional metal element (M1) selected from the group consisting of silver (Ag), gold (Au), zinc (Zn), cadmium (Cd), and tin (Sn).

[0030] In the second cathode electrode, like the first cathode electrode, the second layer covers at least a part of a region of a surface of the first layer, and therefore the second layer has a function as a protective layer for the first layer. In the second cathode electrode, the second layer is also formed continuously to the first layer, and directly contacted on the surface of the first layer. In the second cathode electrode, the second layer also contains the constituent element (M2) having reduction ability composed of at least one metal element selected from the group consisting of copper (Cu), silver (Ag), gold (Au), zinc (Zn), cadmium (Cd), and tin (Sn), and therefore the second layer also functions as a layer having a catalytic ability to reduce carbon dioxide. In the second cathode electrode, there is also a boundary between the first layer and the second layer, and thus the first layer and the second layer can be distinguished by microscope observation or the like.

[0031] The second cathode electrode also has the similar function as the aforementioned first cathode electrode. Therefore, in the second cathode electrode, the selectivity of hydrogen decreases and the selectivity of the carbon dioxide reduction product increases in the above catalytic reaction.

[0032] An aspect of the additional metal element (M1) in the first layer of the cathode electrode is not particularly limited. For example, an aspect of metal itself (metal simple substance) can be mentioned, and in addition to the aspect of metal itself (metal simple substance), an aspect of hydroxide and an aspect of oxide can be mentioned. In the additional metal element (M1), the aspect of metal itself (metal simple substance), the aspect of hydroxide, and the aspect of oxide may be

mixed. Although any of silver, gold, zinc, cadmium, and tin can be used as the additional metal element (M1), zinc and silver are preferable, and zinc is particularly preferable from the viewpoint of more certainly decreasing the selectivity of the hydrogen and more certainly increasing the selectivity of the carbon dioxide reduction product in the catalytic reaction producing carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol with the reduction reaction of carbon dioxide. These additional metal elements (M1) may be used singly, and may be used in combination of two or more thereof. Advantageous effects of the additional metal element (M1) are increase in the stability of the production reaction of the olefinic hydrocarbon such as ethylene or the alcohol such as ethanol reaction and reduction ability of CO_2 to CO. The additional metal element (M1) includes both of a metal element added as a raw material and a metal element deposited by the electrodeposition and the like.

[0033] The number of moles of the copper element relative to the number of moles of the oxygen element in the first layer, that is, the value of the number of moles of the copper element / the number of moles of the oxygen element is not particularly limited, but it is preferable that a lower limit thereof be 1.5, it is more preferable that it be 1.6 from the viewpoint of certainly decreasing the selectivity of hydrogen and certainly increasing the selectivity to the carbon dioxide reduction product, and it is particularly preferable that it be 2.0 from the viewpoint of further decreasing the selectivity of hydrogen and further certainly increasing the selectivity to the carbon dioxide reduction product. Meanwhile, it is preferable that the upper limit of the value of the number of moles of the copper element / the number of moles of the oxygen element be 5.1, it is more preferable that it be 5.0, and it is particularly preferable that is be 4.8 from the viewpoint of ability to stably sustain the catalytic reaction producing carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol with the reduction reaction of carbon dioxide.

[0034] A structure of the first layer of the first cathode electrode may be solid and may be porous, but it is preferable that it be a porous structure from the viewpoint of ability to further stably sustain the catalytic reaction producing carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol with the reduction reaction of carbon dioxide over a long term, certainly increasing the selectivity to the carbon dioxide reduction product, and certainly decreasing the hydrogen selectivity. A proportion of gaps (porosity) in the porous structure is not particularly limited, but it is preferable that a lower limit thereof be 1 vol% and it is particularly that it be 10 vol% from the viewpoint of facilitation of penetration of carbon dioxide into the first layer to further increase the production efficiencies of producing carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol. Meanwhile, it is preferable that an upper limit of the porosity of the porous structure be 99 vol% and it is particularly preferable that it be 90 vol% from the viewpoint of sustaining a surface area contributing to the catalytic reaction of the first layer to further increase the production efficiencies of producing carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol.

[0035] An aspect of the constituent element (M2) having reduction ability in the second layer of the cathode electrode is not particularly limited. For example, an aspect of metal itself (metal simple substance) can be mentioned, and in addition to the aspect of metal itself (metal simple substance), an aspect of hydroxide and an aspect of oxide can be mentioned. In the constituent element (M2) having the reduction ability, the aspect of metal itself (metal simple substance), the aspect of hydroxide, and the aspect of oxide may be mixed. Although any of copper, silver, gold, zinc, cadmium, and tin can be used as the constituent element (M2) having reduction ability, silver, gold, and zinc are preferable, and silver is particularly preferable from the viewpoint of more certainly decreasing the selectivity of the hydrogen and more certainly increasing the selectivity of the carbon dioxide reduction product in the catalytic reaction producing carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol with the reduction reaction of carbon dioxide.

[0036] An average thickness of the second layer is not particularly limited, but it is preferable that a lower limit thereof be 10 nm from the viewpoint of certainly increasing the active sites of the carbon dioxide reduction and certainly inhibiting the decomposition reaction of water, which is the side reaction, due to increase in the amount of water entering the first layer, it is more preferable that it be 20 nm from the viewpoint of further increasing the active sites of the carbon dioxide reduction and further certainly inhibiting the decomposition reaction of water, which is the side reaction, and it is particularly preferable that it be 50 nm from the viewpoint of further increasing the stability. Meanwhile, it is preferable that an upper limit of the average thickness of the second layer be 200 nm from the viewpoint of preventing excessive inhibition of water entering the first layer to enhance the reaction between carbon dioxide and water, certainly increasing the selectivity of the carbon dioxide reduction product, and certainly decreasing the hydrogen selectivity, it is more preferable that it be 180 nm from the viewpoint of further decreasing the hydrogen selectivity, and it is particularly preferable that it be 150 nm from the viewpoint of further increasing the selectivity of the carbon dioxide reduction product and further decreasing the hydrogen selectivity.

[0037] Accordingly, by regulating the average thickness of the second layer within the above range, the active sites of the carbon dioxide reduction certainly increase and the amount of water entering the first layer is certainly regulated within an appropriate range, and therefore the selectivity of the carbon dioxide reduction product certainly increases and the hydrogen selectivity certainly decreases. Note that the average thickness of the second layer means a thickness measured by observing a scanning electron microscope (SEM) image of a cross section of the cathode electrode.

[0038] The cathode electrode of the present invention can electrically reduce carbon dioxide producing carbon

monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol with mainly reacting gaseous carbon dioxide and water by the catalytic action in the first layer by supplying the gaseous carbon dioxide to the cathode electrode from the side of the first layer and supplying water with a liquid phase from the side of the second layer.

[Composite of Cathode Electrode and Substrate]

[0039] The cathode electrode of the present invention may be used in a state of the cathode electrode alone, and may be used in a state of forming a composite with a substrate as described below. FIG. 1 is an explanatory diagram schematically illustrating a cross section of the composite of the cathode electrode and the substrate of the present invention.

[0040] As illustrated in FIG. 1, the composite 120 of the cathode electrode 100 and the substrate 1 has: the substrate 1; and the above cathode electrode 100 of the present invention formed on the substrate 1. The substrate 1 is provided on a side of a first layer 101 of the cathode electrode 100. That is, the side of the first layer 101 of the cathode electrode 100 is disposed on the substrate 1. The substrate is not provided on a side of a second layer 102 of the cathode electrode 100, and the second layer 102 is exposed to an external environment of the cathode electrode 100 and the composite 120. The cathode electrode 100 is a coating film coating a surface of the substrate 1. By containing the cathode electrode 100 of the present invention, the composite 120 of the cathode electrode 100 and the substrate 1 can yield the composite in which the selectivity of hydrogen decreases and the selectivity of the carbon dioxide reduction product increases in the catalytic reaction producing carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol with the reduction reaction of carbon dioxide.

[0041] A structure of the first layer 101 of the cathode electrode 100 formed on the substrate 1 may be solid or may be porous, but as noted above, it is preferable that it be a porous structure from the viewpoint of ability to further stably sustain the catalytic reaction producing carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol with the reduction reaction of carbon dioxide over a long term, certainly increasing the selectivity to the carbon dioxide reduction product, and certainly decreasing the hydrogen selectivity. The porous structure of the first layer 101 of the cathode electrode 100 can be formed by subjecting a cathode electrode having a solid structure to a partial reduction treatment, described later. In FIG. 1, for convenience of description, the first layer 101 is not expressed as the porous structure.

[0042] The substrate 1 has the porous structure in order to smoothly supply gaseous carbon dioxide to the first layer 101. As the substrate 1 having the porous structure, porous carbon, copper (Cu), niobium (Nb), aluminum (Al), titanium (Ti), an alloy containing one or more of the metals, a porous metal composed of metal such as stainless steel, and the like can be mentioned, for example. Among these, the porous carbon is preferable from the viewpoint of ability to smoothly contacting the gaseous carbon dioxide with the first layer 101, further stably sustain the catalytic reaction producing carbon monoxide, the olefinic hydrocarbon such as ethylene, and the alcohol such as ethanol with the reduction reaction of carbon dioxide even with the gaseous carbon dioxide over a long term, certainly increasing the selectivity to the carbon dioxide reduction product, and certainly decreasing the hydrogen selectivity. An average thickness of the substrate 1 is not particularly limited, and a plate material with 0.2 mm or more and 1.5 mm or less can be mentioned, for example.

[0043] The cathode electrode 100 in the composite 120 of the cathode electrode 100 and the substrate 1 is a coelectrodeposition layer formed by, for example, immersing the substrate 1 in a coelectrodeposition solution containing copper ions, which are a raw material of cuprous oxide, and ions of the additional metal element (M1), and coelectrodepositing cuprous oxide and the additional metal element (M1) on the substrate 1.

[Method of Manufacturing Composite of Cathode Electrode and Substrate]

[0044] An example of a method of manufacturing the composite of the cathode electrode and the substrate will be described below. FIG. 2 is an explanatory diagram of the electropolishing treatment step in the method of manufacturing the composite of the cathode electrode and the substrate. FIG. 3 is an explanatory diagram of the coelectrodeposition layer forming step in the method of manufacturing the composite of the cathode electrode and the substrate. FIG. 4 is an explanatory diagram of the partial reduction step in the method of manufacturing the composite of the cathode electrode and the substrate.

[0045] The method of manufacturing the composite of the cathode electrode and the substrate comprises, for example, (1) a step of providing a substrate having a porous structure; (2) an electropolishing treatment step of performing an electropolishing treatment on the provided substrate, if necessary; (3) a first coelectrodeposition layer forming step of coelectrodepositing cuprous oxide and at least one additional metal element (M1) selected from the group consisting of silver, gold, zinc, cadmium, and tin on the substrate in which the electropolishing treatment has been performed if necessary, to form a first coelectrodeposition layer that is the first layer; (4) a second layer forming step of forming a film with a constituent element (M2) composed of at least one metal element selected from the group consisting of copper, silver, gold, zinc, cadmium, and tin to form a second layer on at least a part of a region on the first coelectrodeposition layer; and (5) a partial reduction step of partially reducing the formed first coelectrodeposition layer and second layer, if necessary.

Among the above steps, the step (1), the step (3), and the step (4) are essential steps, and the step (2) and the step (5) are optional steps.

(1) Step of Providing Substrate having Porous Structure

[0046] The step of providing the substrate having a porous structure is a step of providing the above substrate. A type of material of the substrate and a porosity of the porous structure can be appropriately selected depending on required characteristics of the composite of the cathode electrode and the substrate. Among these, as the substrate having the porous structure, porous carbon is preferable.

(2) Electropolishing Treatment Step

[0047] The electropolishing treatment step is a step performed if necessary when metal is used as the material type of the substrate, for example. In the electropolishing treatment step, the substrate surface is degreased with an organic solvent such as hexane, then washed and dried, thereafter as illustrated in FIG. 2, a mixed acid solution 11 is housed in a container 10, a substrate 1, which is a positive electrode, is immersed in the mixed acid solution 11, a negative electrode 2 is immersed at a position sandwiching the substrate 1, and an electrolysis potential is applied between the substrate 1, which is the positive electrode, and the negative electrode 2. By applying the electrolysis potential between the substrate 1, which is the positive electrode, and the negative electrode 2, the surface of the substrate 1 is electropolished. By electropolishing the surface of the substrate 1, the process-modified layer on the surface of the substrate 1 is decreased or removed. As the mixed acid solution 11, an aqueous mixed acid solution of phosphoric acid and sulfuric acid can be mentioned, for example. As the negative electrode 2, titanium can be mentioned, for example.

(3) First Coelectrodeposition Layer Forming Step

[0048] As illustrated in FIG. 3, a coelectrodeposition aqueous solution 21 containing copper ions, the additional metal element (M1), and an organic acid at a predetermined molar ratio are housed in a container 20, and a pH of the coelectrodeposition aqueous solution 21 is adjusted within a predetermined range by using an alkaline aqueous solution. By adjusting a temperature of a medium 23, such as water, in which the outer surface of the container 20 is immersed with a temperature controller 22, a temperature of the coelectrodeposition aqueous solution 21 is adjusted to 50 to 60°C. Then, the substrate 1, a reference electrode (Ag/AgCl) 24, and a counter electrode (platinum electrode) 25 are immersed in the coelectrodeposition aqueous solution 21. Thereafter, by coelectrodepositing cuprous oxide and the additional metal element (M1) on the substrate 1 with controlling a current density supplied from the power source, the first coelectrodeposition layer that is the first layer is formed. An electrodeposited amount, component ratio, and the like of cuprous oxide and additional metal element (M1) to be coelectrodeposited are adjustable by controlling a concentration and component ratio of the coelectrodeposition aqueous solution 21, a time of the coelectrodeposition, the current density, and the pH of the coelectrodeposition aqueous solution 21. As the alkaline aqueous solution, an aqueous sodium hydroxide solution, an aqueous potassium hydroxide solution, and the like can be mentioned, for example. As the set range of the pH, 9.0 to 11 can be mentioned, for example. As the organic acid, oxalic acid, acetic acid, lactic acid, and citric acid can be mentioned, for example.

(4) Second Layer Forming Step

[0049] A method of forming the second layer is not particularly limited, and for example, the second layer can be formed by subjecting the first coelectrodeposition layer that is the first layer to a film forming treatment such as sputtering. The method of film-forming the second layer may be the second coelectrodeposition layer forming step of forming a coelectrodeposition layer by coelectrodeposition. The second coelectrodeposition layer forming step can be performed similarly to the first coelectrodeposition layer forming step illustrated in FIG. 3. That is, a coelectrodeposition aqueous solution 21 containing the constituent element (M2) having reduction ability and an organic acid at a predetermined molar ratio are housed in a container 20, and a pH of the coelectrodeposition aqueous solution 21 is adjusted within a predetermined range by using an alkaline aqueous solution. A temperature of a medium 23, such as water, in which the outer surface of the container 20 is immersed is adjusted with a temperature controller 22. Then, the composite 1' obtained by forming the first coelectrodeposition layer on the substrate 1, a reference electrode (Ag/AgCl) 24, and a counter electrode (platinum electrode) 25 are immersed in the coelectrodeposition aqueous solution 21. Thereafter, by coelectrodepositing constituent element (M2) having reduction ability on the first coelectrodeposition layer with controlling a current density supplied from the power source, the second coelectrodeposition layer that is the second layer is formed. An electrodeposited amount of the constituent element (M2) having reduction ability to be coelectrodeposited, and the like can be adjusted by controlling a concentration of the coelectrodeposition aqueous solution 21, a time of the coelec-

trodeposition, the current density, and the pH of the coelectrodeposition aqueous solution 21.

(5) Partial Reduction Step

[0050] As illustrated in FIG. 4, a composite 1' obtained by forming the first coelectrodeposition layer and the second layer, on the substrate 1, and an anode electrode 33 are immersed in an aqueous solution for the partial reduction 32 housed in a two-chamber type electrolysis cell 30 having a diaphragm 31, and by applying an electrolysis potential from a power source 34 to the two-chamber type electrolysis cell 30, the partial reduction treatment is performed. By performing the partial reduction treatment, the first coelectrodeposition layer that is the first layer can become porous. As the anode electrode 33, platinum can be mentioned, for example. As the aqueous solution for the partial reduction 32, an aqueous potassium hydrogen carbonate solution can be mentioned on both the composite 1' side and the anode electrode side, for example.

[Electrolytic Reduction Apparatus]

[0051] Thereafter, an electrolytic reduction apparatus that electrically reduces carbon dioxide to carbon monoxide, an olefinic hydrocarbon, and/or an alcohol, which has the cathode electrode of the present invention, and an electrolytic reduction apparatus that electrically reduces carbon dioxide to carbon monoxide, an olefinic hydrocarbon, and/or an alcohol, which has the composite of the cathode electrode and the substrate of the present invention, will be described below. FIG. 5 is an explanatory diagram illustrating an outline of the electrolytic reduction apparatus having the cathode electrode of the present invention.

[0052] As illustrated in FIG. 5, as an electrolytic reduction apparatus 210, a three-chamber type electrolytic reduction apparatus can be mentioned, for example. Specifically, the electrolytic reduction apparatus 210 has, for example, an electrolysis cell 214 having a cathode gas chamber 211, a cathode liquid chamber 212, and an anode liquid chamber 213, which are divided from each other. The cathode gas chamber 211 and the cathode liquid chamber 212 are divided by a cathode 216 as a gas diffusion electrode. The cathode liquid chamber 212 and the anode liquid chamber 213 are divided by a diaphragm 217 having ion conductivity. An anode 218 is disposed in the anode liquid chamber 213. Into the cathode gas chamber 211, carbon dioxide gas is supplied. Into the cathode liquid chamber 212, a cathode liquid is supplied. Into the anode liquid chamber 213, an anode liquid is supplied. The anode 218 and the cathode 216 are connected to a direct-current power source 219.

[0053] The anode liquid and the cathode liquid are aqueous solutions in which an electrolyte is dissolved. The electrolyte contains at least one of potassium, sodium, lithium, or compounds of these. The electrolyte preferably contains at least one selected from the group consisting of LiOH, NaOH, KOH, Li_2CO_3, Na_2CO_3, K_2CO_3, LiHCOa, NaHCOa, and $KHCO_3$, for example.

[0054] The cathode 216 is a gas diffusion electrode, and has a gas diffusion layer 221 and a micro-porous layer 222. In the electrolytic reduction apparatus 210, the composite of the cathode electrode and the substrate of the present invention is used as the cathode 216, and the micro-porous layer 222 corresponds to the substrate of the composite. The gas diffusion layer 221 allows gas including carbon dioxide to permeate, but inhibits permeation of the aqueous solution including the cathode liquid. The micro-porous layer 222 allows both the gas including carbon dioxide and the aqueous solution including the cathode liquid to permeate. The gas diffusion layer 221 and the micro-porous layer 222 are each formed in a plane shape. The gas diffusion layer 221 is disposed on a side of the cathode gas chamber 211, and the micro-porous layer 222 is disposed on a side of the cathode liquid chamber 212.

[0055] As the gas diffusion layer 221, a layer in which a water-repellent coating such as polytetrafluoroethylene is formed on a surface of a porous conductive substrate such as carbon paper, carbon felt, and carbon cloth can be mentioned, for example. The conductive substrate is connected to a negative electrode of the direct-current power source 219, and electrons are supplied. The micro-porous layer 222 is formed on a surface of the gas diffusion layer 221 by using carbon black or the like, and supports a catalyst. In the electrolytic reduction apparatus 210, the cathode electrode of the present invention is used as the catalyst which the micro-porous layer 222 supports.

Examples

[0056] Thereafter, Examples of the present invention will be described. The present invention is not limited to the following Examples.

[Example 1]

Preparation of Cathode Electrode

First Coelectrodeposition Layer Forming Step

[0057] With the coelectrodeposition apparatus illustrated in FIG. 3, a temperature of a coelectrodeposition aqueous solution mainly containing copper sulfate and zinc sulfate whose pH was adjusted to 9.5 to 10 by using an aqueous sodium hydroxide solution was adjusted to 50 to 60°C by adjusting a temperature of water, which was a medium, with a temperature controller, then a substrate (porous carbon), a reference electrode (Ag/AgCl), and a counter electrode (platinum electrode) were installed in the coelectrodeposition aqueous solution, and by coelectrodepositing copper, cuprous oxide, and zinc (an aspect of hydroxide and/or oxide) on the substrate with controlling the current density, a first coelectrodeposition layer, which corresponded to the first layer, was formed on the substrate.

Second Layer Forming Step

[0058] The first coelectrodeposition layer, which was the first layer, was subjected to a sputtering treatment to form the second layer with 10 nm in average thickness on the first coelectrodeposition layer, which was the first layer to manufacture a composite of a cathode electrode and a substrate.

Partial Reduction Step

[0059] On the first coelectrodeposition layer and the second layer formed on the substrate, with a two-chamber type electrolysis cell having a diaphragm illustrated in FIG. 4, the partial reduction treatment was performed on the first coelectrodeposition layer to allow the first coelectrodeposition layer to be porous by electrolysis using platinum as the anode electrode and the aqueous potassium hydrogen carbonate solution as aqueous solutions for the partial reduction on both the substrate side on which the first coelectrodeposition layer was formed and the anode electrode side.

[Example 2]

[0060] A composite of a cathode electrode and a substrate was manufactured in the same manner as in Example 1 except that the second layer was formed in 100 nm in average thickness by controlling the conditions of the sputtering treatment.

[Example 3]

[0061] A composite of a cathode electrode and a substrate was manufactured in the same manner as in Example 1 except that the second layer was formed in 200 nm in average thickness by controlling the conditions of the sputtering treatment.

[Comparative Example 1]

[0062] A composite of a cathode electrode and a substrate was manufactured in the same manner as in Example 1 except that the second coelectrodeposition layer forming step was not performed and the second layer, which was the protective layer, was not formed.

[0063] The additional metal element (M1), the constituent element (M2) having reduction ability, the average thickness of the second layer, and the value of the number of moles of the copper element / the number of moles of the oxygen element (Cu/O ratio) in the first layer of the Examples and Comparative Example are shown in the following Table 1.

Evaluation Items

[Stability Test]

[0064] A change with time of a total selectivity of the carbon dioxide reduction production gas was measured as described later. Based on a time when the total selectivity of the carbon dioxide reduction production gas was started to drop, a time from the base time until the total selectivity of the carbon dioxide reduction production gas dropped to 95% of the base was specified as an index of stability.

[Total Selectivity of Carbon Dioxide Reduction Production Gas (%)]

[0065] From a concentration of the product contained in an output gas of the electrolysis cell and the gas flow rate, the number of moles of the product and the number of moles of required electrons per unit time were calculated. Meanwhile, from the set current value of the potential applying apparatus, the number of moles of electrons that passed through the electrolysis cell per unit time was calculated. A proportion of the former to the latter was evaluated as the total selectivity of the carbon dioxide reduction production gas (%). The concentration of the product contained in the output gas was measured by using a gas chromatograph (model number: Agilent 990 micro GC). The gas flow rate was measured by using a mass flow meter. The total selectivity of the carbon dioxide reduction production gas refers to a total value of selectivity of gas components, in the product, reduced from carbon dioxide. As the gas components, ethylene, methane, carbon monoxide, ethane, and the like can be mentioned.

[Hydrogen Selectivity (%)]

[0066] A proportion of hydrogen in the product by the measurement of the total selectivity of the carbon dioxide reduction production gas was measured as the selectivity (%).

[0067] Measurement results of Examples and Comparative Example are shown in the following Table 1.

[Table 1]

	Additional metal element (M1)	Constituent element (M2) having reduction ability	Average thickness of second layer (nm)	Cu/O ratio	Total selectivity of carbon dioxide reduction production gas (%)	Hydrogen selectivity (%)	Stability (min)
Comparative Example 1	Zn	-	0	6,5	57	34	630
Example 1	Zn	Ag	10	5,1	72	23	660
Example 2	Zn	Ag	100	3,6	70	15	960
Example 3	Zn	Ag	200	1,5	59	31	1230

[0068] As shown in the Table 1, in Examples 1 to 3 in which the second layer functioning as the protective layer coated the first layer functioning as the catalyst layer, the hydrogen selectivity decreased and the total selectivity of the carbon dioxide reduction production gas increased in the catalyst reaction producing ethylene and carbon monoxide with the reduction reaction of carbon dioxide.

[0069] Particularly, in Examples 2 to 3 in which the average thickness of the second layer was within a range of 100 nm to 200 nm, the stability of ability in which the catalytic reaction was stably sustained over a long term increased. In Examples 2 to 3 in which the Cu/O ratio was within a range of 1.5 to 3.6, the stability increased. In Examples 1 to 3, the total selectivity of the carbon dioxide reduction production gas (%) further increased and the hydrogen selectivity (%) further decreased by using the silver element as the constituent element (M2) having reduction ability.

[0070] Meanwhile, in Comparative Example 1 in which the second layer functioning as the protective layer was not formed on the first layer functioning as the catalyst layer, the hydrogen selectivity did not sufficiently decrease and excellent total selectivity of the carbon dioxide reduction production gas was not obtained in the above catalytic reaction.

Industrial Applicability

[0071] The cathode electrode of the present invention can sustain the catalytic reaction producing the olefinic hydrocarbon such as ethylene and the alcohol such as ethanol by the reduction reaction of carbon dioxide with high efficiency; thus, it has high utility value in the field where carbon dioxide in the atmosphere is absorbed and recovered to produce industrially useful organic compounds from the carbon dioxide.

List of Reference Signs

[0072]

1 substrate

100 cathode electrode
101 first layer
102 second layer
120 composite

Claims

1. A cathode electrode that electrically reduces carbon dioxide, comprising:

   a first layer containing cuprous oxide, copper, and at least one additional metal element selected from the group consisting of silver, gold, zinc, cadmium, and tin; and
   a second layer formed on at least a part of a region on the first layer and containing a constituent element composed of at least one metal element selected from the group consisting of copper, silver, gold, zinc, cadmium, and tin.

2. A cathode electrode that electrically reduces carbon dioxide, comprising:

   a first layer containing cuprous oxide and at least one additional metal element selected from the group consisting of silver, gold, zinc, cadmium, and tin; and
   a second layer formed on at least a part of a region on the first layer and containing a constituent element composed of at least one metal element selected from the group consisting of copper, silver, gold, zinc, cadmium, and tin.

3. The cathode electrode according to claim 2, wherein a part of cuprous oxide in the first layer is reduced to copper by a reduction treatment.

4. The cathode electrode according to claim 1 or 2, wherein the second layer is a protective layer for the first layer.

5. The cathode electrode according to claim 1 or 2, wherein the constituent element of the second layer contains a silver element.

6. The cathode electrode according to claim 5, wherein the silver element as the constituent element is in a state of simple substance of silver or an oxide of silver.

7. The cathode electrode according to claim 1 or 2, wherein the additional metal element of the first layer contains a zinc element.

8. The cathode electrode according to claim 1 or 2, wherein an average thickness of the second layer is 10 nm or more and 200 nm or less.

9. The cathode electrode according to claim 1 or 2, wherein a value of the number of moles of a copper element / the number of moles of an oxygen element in the first layer is 1.5 or more and 5.1 or less.

10. The cathode electrode according to claim 1 or 2, wherein the first layer has a porous structure.

11. A composite of a cathode electrode and a substrate, comprising: a substrate having a porous structure; and the cathode electrode according to claim 1 or 2 in which a side of the first layer is disposed on the substrate.

12. The composite according to claim 11, wherein the substrate is porous carbon.

13. An electrolytic reduction apparatus that electrically reduces carbon dioxide to carbon monoxide, an olefinic hydrocarbon, and/or an alcohol, comprising the cathode electrode according to claim 1 or 2.

14. An electrolytic reduction apparatus that electrically reduces carbon dioxide to carbon monoxide, an olefinic hydrocarbon, and/or an alcohol, comprising the composite according to claim 11.

15. A method of manufacturing a composite of a cathode electrode and a substrate, comprising:

a step of providing a substrate having a porous structure;
a first coelectrodeposition layer forming step of coelectrodepositing cuprous oxide and at least one additional metal element selected from the group consisting of silver, gold, zinc, cadmium, and tin on the substrate to form a first coelectrodeposition layer that is a first layer; and
a second layer forming step of forming a film with a constituent element composed of at least one metal element selected from the group consisting of copper, silver, gold, zinc, cadmium, and tin to form a second layer on at least a part of a region on the first coelectrodeposition layer.

16. The manufacturing method according to claim 15, further comprising a partial reduction step of partially reducing the first coelectrodeposition layer and the second layer after the second layer forming step.

17. The manufacturing method according to claim 15 or 16, wherein the substrate is porous carbon.

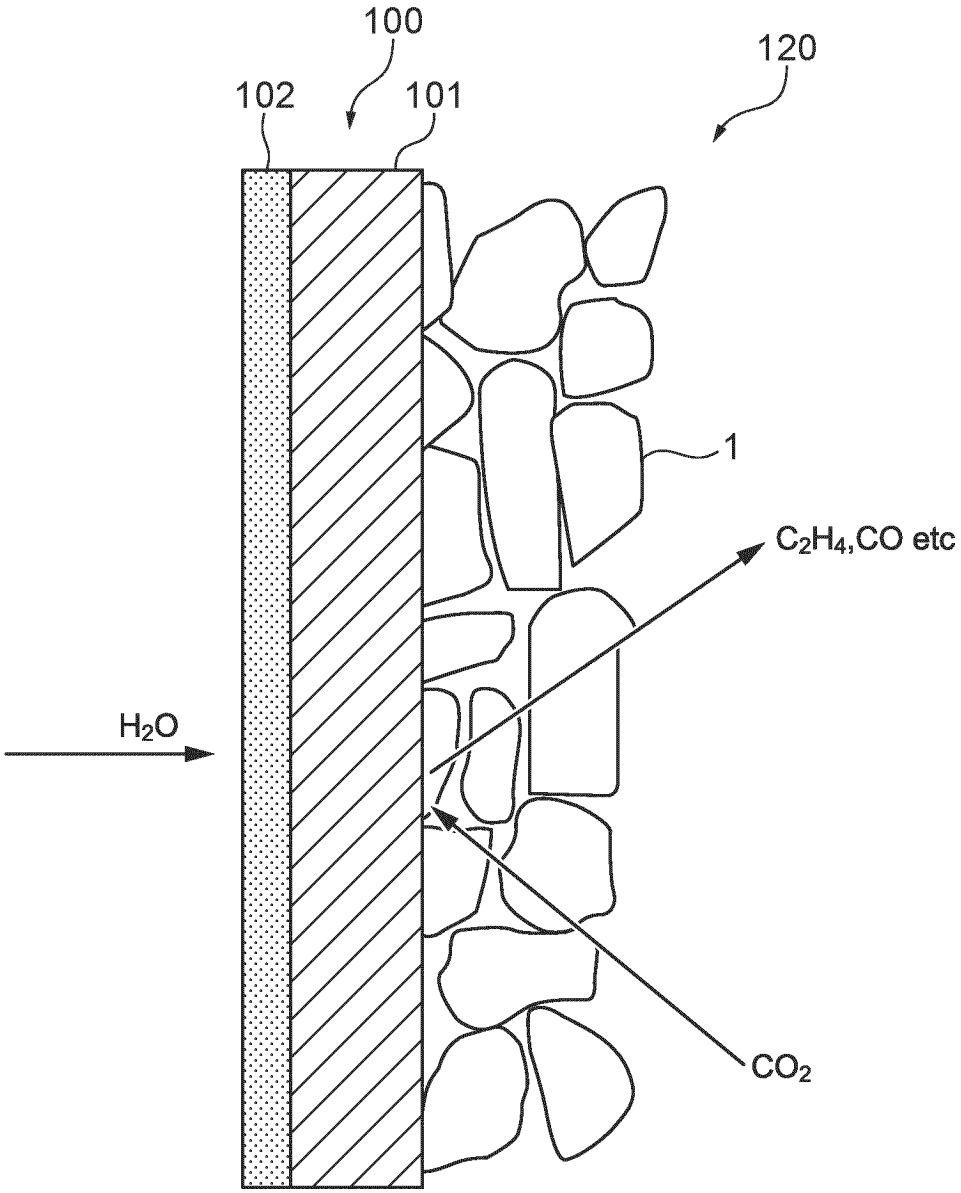


FIG.1

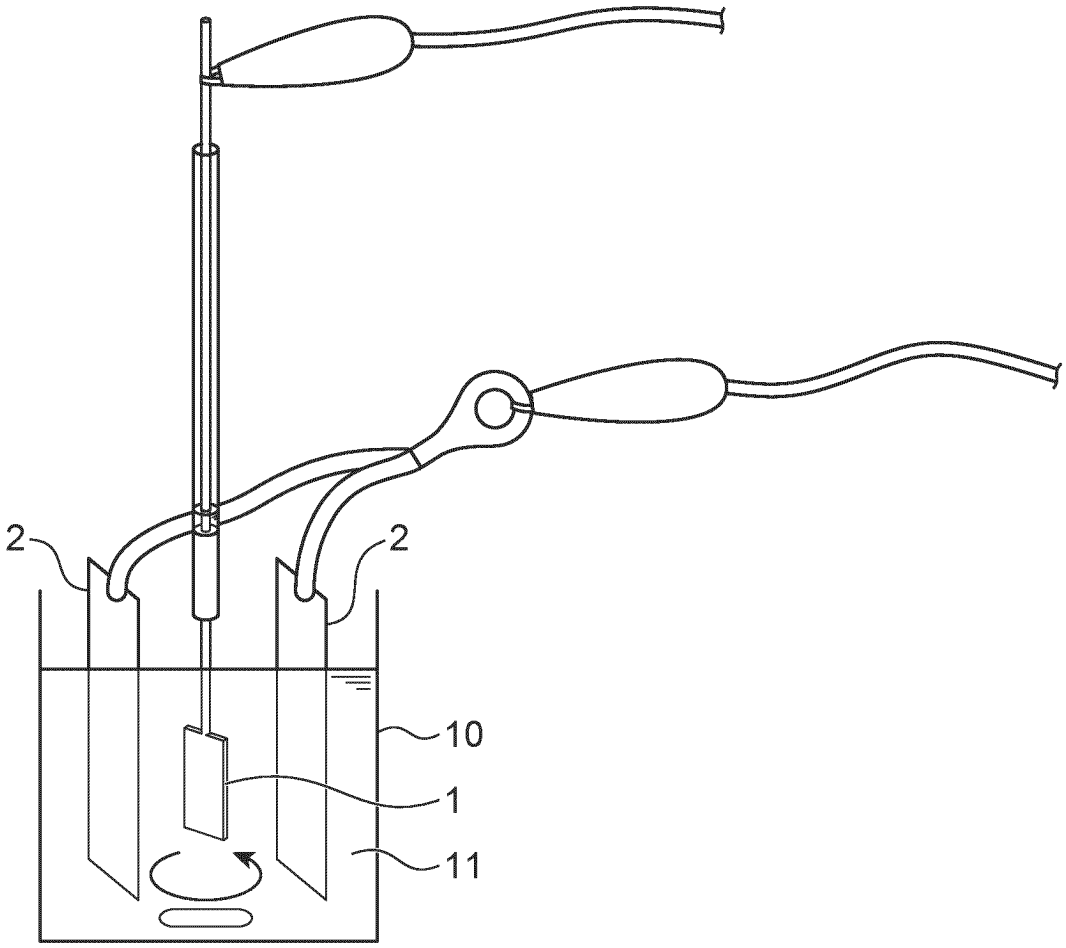


FIG.2

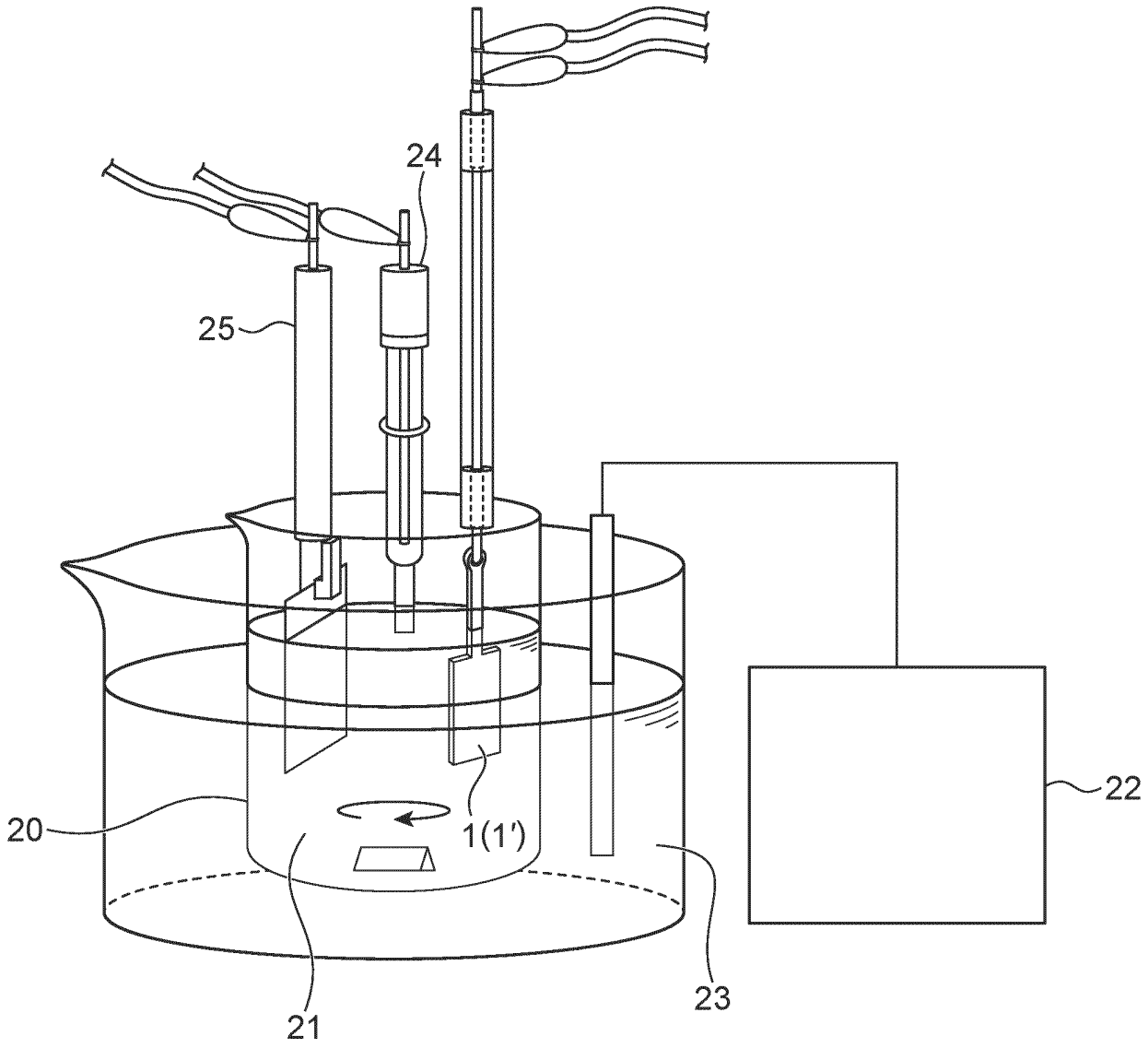


FIG.3

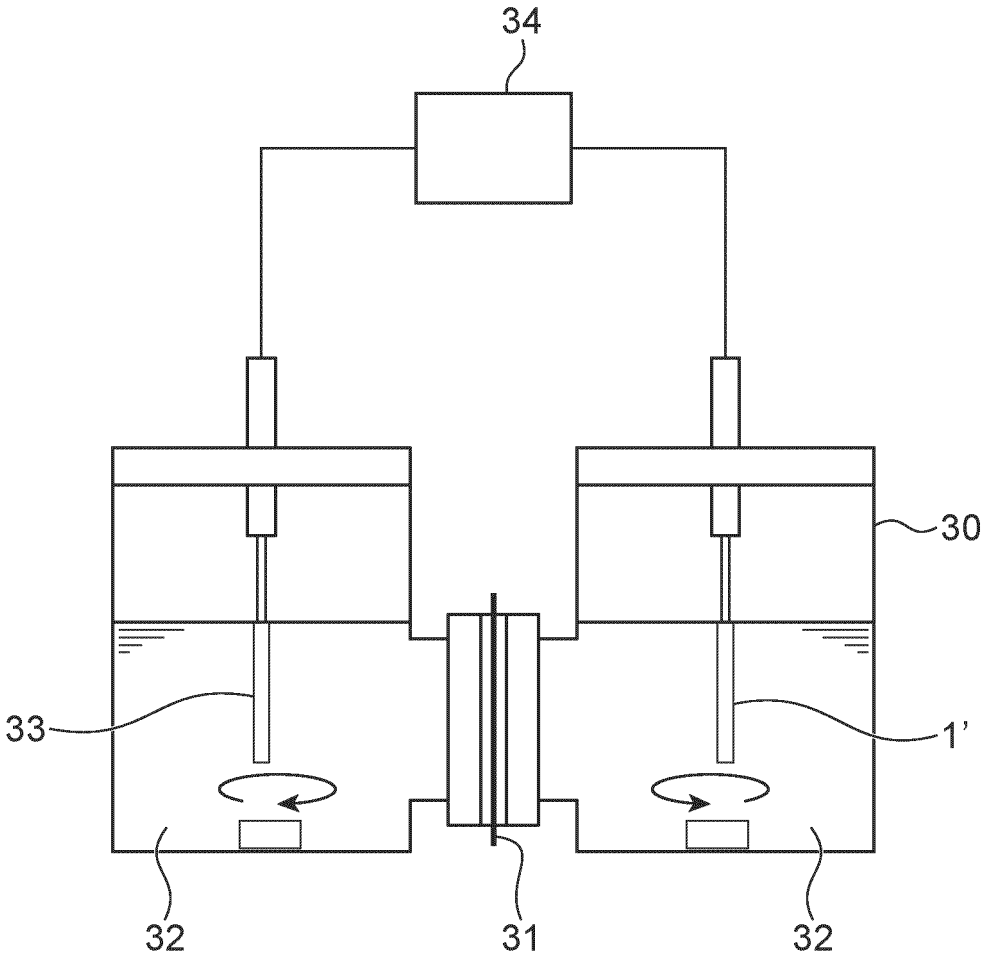
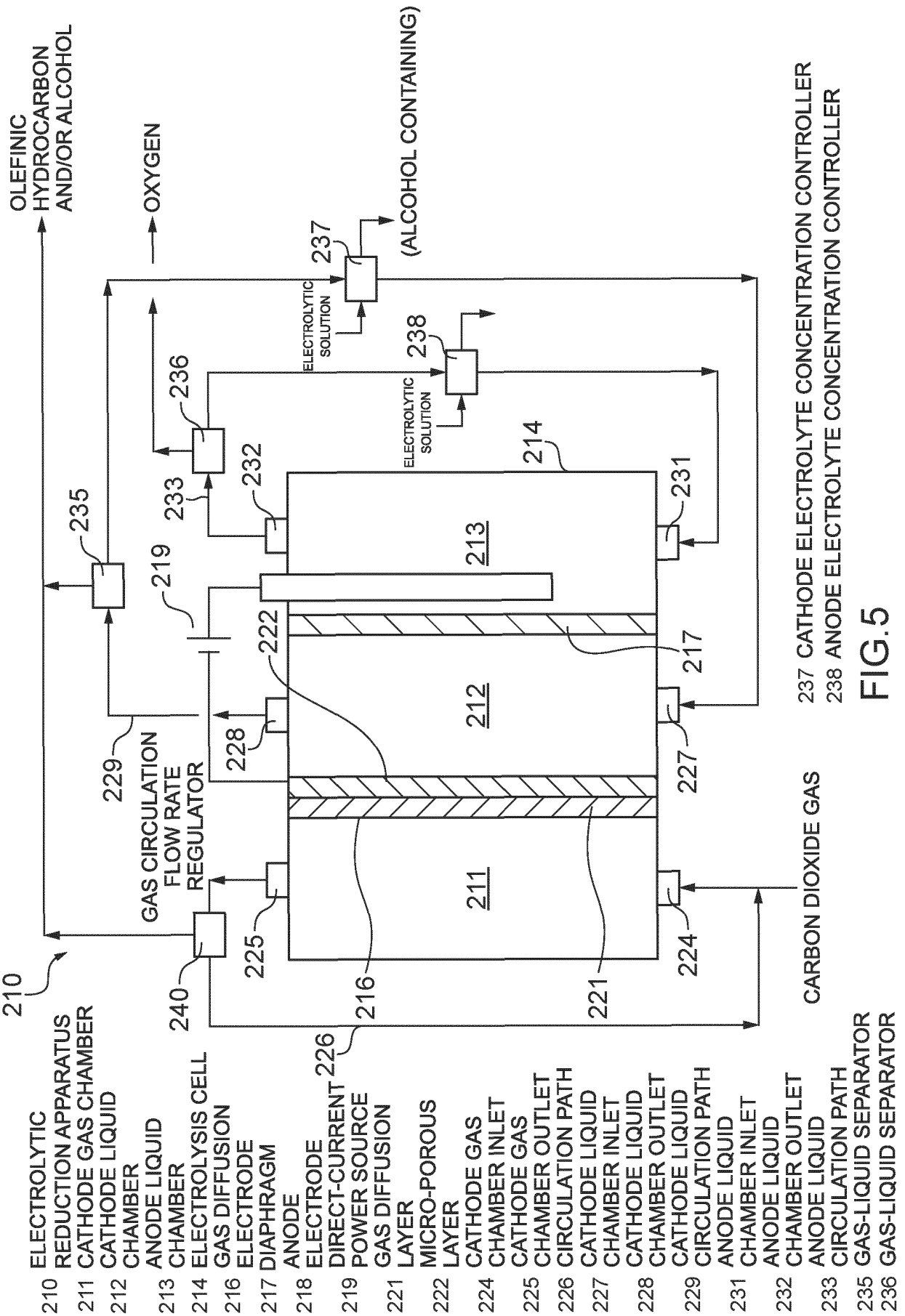


FIG.4



210 ELECTROLYTIC REDUCTION APPARATUS
211 CATHODE GAS CHAMBER
212 CATHODE LIQUID CHAMBER
213 ANODE LIQUID CHAMBER
214 ELECTROLYSIS CELL
216 GAS DIFFUSION ELECTRODE
217 DIAPHRAGM
218 ANODE ELECTRODE
219 DIRECT-CURRENT POWER SOURCE
221 GAS DIFFUSION LAYER
222 MICRO-POROUS LAYER
224 CATHODE GAS CHAMBER INLET
225 CATHODE GAS CHAMBER OUTLET
226 CIRCULATION PATH CATHODE LIQUID
227 CHAMBER INLET CATHODE LIQUID
228 CHAMBER OUTLET CATHODE LIQUID
229 CIRCULATION PATH ANODE LIQUID
231 CHAMBER INLET ANODE LIQUID
232 CHAMBER OUTLET ANODE LIQUID
233 CIRCULATION PATH GAS-LIQUID SEPARATOR
235 GAS-LIQUID SEPARATOR
236
237 CATHODE ELECTROLYTE CONCENTRATION CONTROLLER
238 ANODE ELECTROLYTE CONCENTRATION CONTROLLER

FIG.5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/000517

A. CLASSIFICATION OF SUBJECT MATTER

C25B 11/091(2021.01)i; ***C25B 1/23***(2021.01)i; ***C25B 3/03***(2021.01)i; ***C25B 3/07***(2021.01)i; ***C25B 3/26***(2021.01)i; ***C25B 9/00***(2021.01)i; ***C25B 11/031***(2021.01)i; ***C25B 11/053***(2021.01)i; ***C25B 11/065***(2021.01)i; ***C25B 11/075***(2021.01)i; ***C25B 11/081***(2021.01)i; ***C25B 11/093***(2021.01)i

FI: C25B11/091; C25B11/053; C25B11/031; C25B11/065; C25B11/075; C25B1/23; C25B3/03; C25B3/07; C25B3/26; C25B9/00 Z; C25B9/00 G; C25B11/093; C25B11/081

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C25B11/091; C25B1/23; C25B3/03; C25B3/07; C25B3/26; C25B9/00; C25B11/031; C25B11/053; C25B11/065; C25B11/075; C25B11/081; C25B11/093

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

JSTPlus/JMEDPlus/JST7580 (JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2021/153503 A1 (RIKEN) 05 August 2021 (2021-08-05) claims, paragraphs [0026], [0032], [0041], [0070], table 1, examples 6, 13	1-4, 7, 9-10, 13
Y		1-4, 7-17
A		5-6
Y	JP 2018-24895 A (THE FURUKAWA ELECTRIC CO., LTD.) 15 February 2018 (2018-02-15) claims, paragraphs [0028], [0030], [0084]	1-4, 7-17
A		5-6
Y	CN 109594100 A (NATIONAL DONG HWA UNIVERSITY) 09 April 2019 (2019-04-09) claims, examples, paragraphs [0006], [0009]-[0023]	1-6, 11-15, 17
A		7-10, 16

☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 March 2023	**28 March 2023**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2023/000517

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2021/0115577 A1 (UNIVERSITY OF CINCINNATI) 22 April 2021 (2021-04-22) claims, fig. 1A, paragraphs [0032], [0041]	1-6, 11-15, 17
A		7-10, 16

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/000517

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2021/153503 A1	05 August 2021	US 2022/0356588 A1 claims, paragraphs [0055], [0062], [0075]-[0076], [0111], table 1, examples 6, 13 CN 115053021 A	
JP 2018-24895 A	15 February 2018	(Family: none)	
CN 109594100 A	09 April 2019	(Family: none)	
US 2021/0115577 A1	22 April 2021	(Family: none)	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2018168410 A **[0008]**

Non-patent literature cited in the description

- **Y HORI**. Electrochemical reduction of CO at a Copper Electrode. *J. Phys. Chem. B.*, 1997, vol. 101 (36), 7075-7081 **[0009]**