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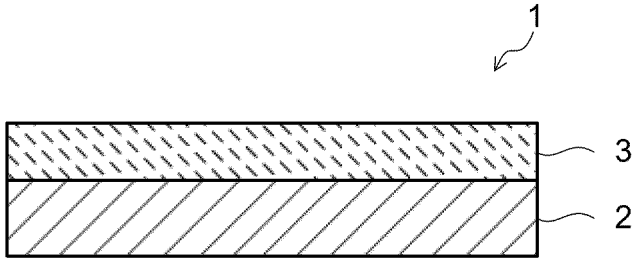
(54) ELECTRODE CATALYST LAYER FOR ELECTROLYSIS CELL, ELECTRODE FOR ELECTROLYSIS CELL, AND CARBON DIOXIDE ELECTROLYTIC DEVICE

(57) An electrode catalyst layer for electrolytic cell 3 of an embodiment includes: a carbon material; a metal catalyst supported on the carbon material; and a water-repellent organic substance. In the electrode catalyst layer for electrolytic cell of the embodiment, the water-repellent organic substance includes an organic substance containing sulfur. A metal-sulfur bond is formed between the organic substance containing sulfur and the metal catalyst. A mass ratio (S/M) of a sulfur element (S) to a metal element (M) in the metal catalyst in the catalyst layer is not less than 0.03 nor more than 0.1.

FIG. 1



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Description

FIELD

[0001] Embodiments described herein relate generally to an electrode catalyst layer for electrolytic cell, an electrode for electrolytic cell, and a carbon dioxide electrolytic device.

BACKGROUND

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

[0003] As devices which produce the chemical substances using the renewable energy such as sunlight, for example, there is known an electrolytic device which reduces carbon dioxide (CO_2) generated from a power plant, an incinerator, or the like. A CO_2 electrolytic device includes a cathode (reduction electrode) which reduces CO_2 to produce a carbon compound such as carbon monoxide (CO) and an anode (oxidation electrode) which oxidizes water (H_2O) or a hydroxide ion (OH^-). It is effective to apply, to such a CO_2 electrolytic device, a cell shape (electrolytic cell) in which the cathode and the anode are stacked with a permeable membrane such as an ion exchange membrane interposed therebetween, and direct supply of CO_2 to a cathode catalyst layer of the electrolytic cell allows a reduction reaction of CO_2 to rapidly progress. Such an electrolytic cell is required, by controlling a structure of the cathode catalyst layer appropriately, for a catalyst reaction in the cathode to be improved and made more efficient, and for performance of the electrolytic cell to be maintained for a long period of time.

SUMMARY

[0004] A subject be solved by the aspect of the present invention is to provide an electrode catalyst layer for electrolytic cell, an electrode for electrolytic cell, and a carbon dioxide electrolytic device which make it possible to cause a catalyst reaction in a reduction electrode (cathode) in the carbon dioxide electrolytic device to be improved and made more efficient, and to maintain performance of an electrolytic cell for a long period of time.

[0005] According to the aspects of the present invention, there is provided an electrode catalyst layer for electrolytic cell, an electrode for electrolytic cell, and a carbon dioxide electrolytic device which make it possible to cause a catalyst reaction in a reduction electrode in the carbon dioxide electrolytic device to be improved and made more efficient, and to maintain performance of an electrolytic cell for a long period of time.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006]

FIG. 1 illustrates an electrode for electrolytic cell of an embodiment.
FIG. 2 illustrates a first example of a carbon dioxide electrolytic cell and a carbon dioxide electrolytic device using it of the embodiment.
FIG. 3 illustrates a second example of a carbon dioxide electrolytic cell and a carbon dioxide electrolytic device using it of the embodiment.
FIG. 4 is a chart illustrating time changes in production efficiency of carbon monoxide obtained by using carbon dioxide electrolytic devices in examples and comparative examples.

DETAILED DESCRIPTION

[0007] An electrode catalyst layer for electrolytic cell of carbon dioxide of an embodiment includes: a carbon material; a metal catalyst supported on the carbon material; and a water-repellent organic substance. In the electrode catalyst layer for electrolytic cell of carbon dioxide of the embodiment, the water-repellent organic substance including an organic substance containing sulfur, the organic substance containing sulfur has a metal-sulfur bond formed between the sulfur and the metal catalyst, and a mass ratio (S/M) of a sulfur element (S) to a metal element (M) in the metal catalyst in the catalyst layer is 0.03 or more and 0.1 or less.

[0008] Hereinafter, an electrode catalyst layer and an electrode for electrolytic cell, and a carbon dioxide electrolytic

device of an embodiment will be described with reference to the drawings. Note that in each embodiment, substantially the same components are denoted by the same reference signs, and a description thereof is sometimes partially omitted. The drawings are schematic, and relationships between thicknesses and planar sizes of the respective portions, thickness proportions of the respective portions, and the like are sometimes different from actual ones.

[0009] FIG. 1 illustrates an electrode for electrolytic cell 1 of the embodiment. The electrode 1 is a reduction electrode (cathode) used for reduction of carbon dioxide (CO_2) in the carbon dioxide electrolytic device, and includes a conductive base material 2 and a catalyst layer (electrode catalyst layer) 3 provided on the conductive base material 2. The catalyst layer 3 is a cathode catalyst layer. The conductive base material 2 includes a material containing at least one selected from a group consisting of, for example, titanium, nickel, iron, and carbon. However, the composing material of the conductive base material 2 is not limited to them. The conductive base material 2 is preferably a base material having a porous structure such as a mesh material, a punched material, a porous body, or a metal fiber sintered compact similarly to the later-described catalyst layer 3, and makes it easy that diffusion of gas, discharge of water, and the like occur.

[0010] The carbon dioxide electrolytic device using the electrode for electrolytic cell 1 of the embodiment reduces carbon dioxide (CO_2) to produce a carbon compound in the cathode (reduction electrode) and oxidizes water (H_2O) or a hydroxide ion (OH^-) to produce oxygen (O_2) in an anode (oxidation electrode), as described later. As the carbon compound produced in the cathode, there can be cited carbon monoxide (CO), methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), methanol (CH_3OH), ethanol (C_2H_5OH), ethylene glycol ($C_2H_6O_2$), or the like.

[0011] The catalyst layer 3 includes a carbon material, a metal catalyst supported on the carbon material, and a water-repellent organic substance. In such a catalyst layer 3, the water-repellent organic substance includes an organic substance containing sulfur, and a metal-sulfur bond is formed between the organic substance containing sulfur and the metal catalyst. In the catalyst layer 3, a mass ratio (S/M) of a sulfur element (S) to a metal element (M) in the metal catalyst is set to not less than 0.03 nor more than 0.1. The catalyst layer 3 makes it possible to increase reduction efficiency of CO_2 and production efficiency of the carbon compound such as carbon monoxide (CO) based thereon by using the reduction electrode (cathode) 1, and to maintain the production efficiency of the carbon compound (the production efficiency of CO, or the like) for a long period of time. The mass ratio (S/M) of the sulfur element (S) to the metal element (M) is measured as follows. The metal element (M) content in the solution which the catalyst is dissolved with acid is quantified by an ICP (Inductively Coupled Plasma) optical emission spectrometry. The sulfur element (S) content is quantified by an infrared absorption method after combustion in a high-frequency induction furnace. The mass ratio (S/M) is obtained from the measurement values. Details on the catalyst layer 3 are described below.

[0012] The carbon material in the catalyst layer 3 functions as a support for the metal catalyst, and includes at least one selected from a group consisting of, for example, a carbon particle, a carbon nanotube, activated carbon, and graphene. The carbon material as a catalyst support preferably has a porous structure. As applicable materials, there can be cited carbon black such as ketjen black and Vulcan XC-72 (trade name, manufactured by CABOT CORPORATION), activated carbon, a carbon nanotube, graphene, and so on, for example. The carbon material has the porous structure, thereby increasing an area of an active surface contributing to an oxidation-reduction reaction, which allows an increase in conversion efficiency.

[0013] It is preferable that not only the above-described catalyst support but also the catalyst layer 3 itself formed on the conductive base material 2 has the porous structure and has many relatively large pores. Concretely, it is preferable that a distribution frequency of the pores becomes maximum in a range of a diameter of not less than 5 μm nor more than 200 μm in a pore size distribution of the catalyst layer 3 measured by a mercury intrusion method. In such a case, gas quickly diffuses in the whole catalyst layer 3 and a reduction product is also easily discharged to the outside of the catalyst layer 3 through the path, resulting in allowing the electrode 1 to be efficient.

[0014] To efficiently supply CO_2 to the catalyst layer 3, the conductive base material (electrode base material) 2 supporting the catalyst layer 3 is preferably provided with a gas diffusion layer. The gas diffusion layer is formed of a porous body having conductivity. The gas diffusion layer formed of a water-repellent porous body is preferable because the amount of the water produced by a reduction reaction and the water moved from an oxidation electrode (anode) side can be decreased, the water can be discharged via a gas flow path, and the percentage of a carbon dioxide gas in the porous body can be made large. An extremely small thickness of the gas diffusion layer degrades the uniformity on the cell surface. On the other hand, an extremely large thickness of the gas diffusion layer causes a decrease in efficiency due to an increase in diffusion resistance of gas in addition to an increase in member costs. To further improve diffusibility, providing a denser diffusion layer (mesoporous layer) between the gas diffusion layer and the catalyst layer 3 makes it possible to change water repellency and a porous body degree to promote the diffusibility of gas and the discharge of a liquid component.

[0015] For the metal catalyst supported on the above-described carbon material (support), a material which reduces the hydrogen ion and activation energy for reducing CO_2 is used. In other words, the metal material which reduces an overvoltage when the carbon compound is produced by the reduction reaction of CO_2 is used. It is preferable to use at least one metal selected from a group consisting of, for example, 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), and tin (Sn), an alloy containing the metal, or an oxide of the metal. Without being limited to these, for example, a metal complex such as a Ru complex or a Re complex can also be used as a reduction catalyst. Further, a plurality of materials may be mixed to be used. To the metal catalyst, various shapes such as a particle shape, a plate shape, a mesh shape, a wire shape, a porous shape, a film shape, and an island shape can be applied. Note that despite being referred to as the metal catalyst here, without being limited to materials composed of only metal elements, metal oxides containing the above-described metal elements are applicable.

[0016] The metal catalyst preferably has at least one structure selected from a group consisting of a nanoparticle, a nanostructure, and a nanowire. When a metal nanoparticle is applied to the metal catalyst, its average diameter is preferably not less than 1 nm nor more than 15 nm, more preferably not less than 1 nm nor more than 10 nm, and further preferably not less than 1 nm nor more than 5 nm. Satisfying this condition increases a surface area of metal per catalyst mass to exhibit high activity. The same goes for applying the nanostructure or the nanowire.

[0017] In the catalyst layer 3, a mass of the metal catalyst per unit area is preferably not less than 0.01 mg/cm^2 nor more than 5 mg/cm^2, more preferably not less than 0.01 mg/cm^2 nor more than 3 mg/cm^2, and further preferably not less than 0.01 mg/cm^2 nor more than 1 mg/cm^2. Satisfying this condition is for allowing the catalyst layer 3 to have water repellency therein and to quickly discharge water and a product. A thickness of the catalyst layer is preferably not less than 5 μm nor more than 200 μm. Satisfying this condition allows the reduction reaction of CO_2 caused by the catalyst layer 3 to efficiently occur. The mass of the metal catalyst per unit area is measured as follows. The 10 cm square of segment is cut out of the cathode, and the segment is dissolved with acid, and the metal catalyst content in solution is quantified. The mass of the metal catalyst per unit is obtained from the measurement value. Otherwise, the mass of the metal catalyst may be calculated by the mass increasing in before and after the catalyst layer 3 provided on the electrode base material 2. The thickness of the catalyst layer 3 is measured as follows. The cathode 1 (31), or a stack of the cathode (31), an anode (41) and a separator (50) is cut, and a cross-section is observed by SEM (Scanning Electron Microscope). The arbitrary five fields of SEM images are selected, and thicknesses of the catalyst layer of arbitrary three places in each field are measured. The thicknesses of 15 places in total is averaged, and such a mean value is assumed the thickness of the catalyst layer.

[0018] The organic substance containing sulfur (S) as the water-repellent organic substance is not particularly limited, and any of sulfide, sulfoxide, sulfone, and so on is applicable as a portion containing S. As such an organic substance containing S, for example, thiol, sulfene, thiophene, tetrahydrothiophene, and the like can be used. As a substituent bonded to the organic substance containing S, a substituted or unsubstituted alkyl group, a substituted or unsubstituted alkenyl group, a substituted or unsubstituted alkynyl group, or the like can be used. Moreover, a plurality of unsaturated bonds may be included. A halogen such as F or Cl may be substituted for these substituents.

[0019] As specific examples of the organic substance containing sulfur (S), there can be cited alkanethiol such as methanethiol, ethanethiol, propanethiol, butanethiol, pentanethiol, hexanethiol, heptanethiol, octanethiol, nonanethiol, decanethiol, undecanethiol, or dodecanethiol, and alkanesulfene such as methanesulfene, ethanesulfene, propanesulfene, butanesulfene, pentanesulfene, hexanesulfene, heptanesulfene, octanesulfene, nonanesulfene, decanesulfene, undecanesulfene, or dodecanesulfene. These are not restrictive.

[0020] Thiophene is not limited to thiophene (C_4H_4S) itself, and may be a thiophene derivative in which a substituent is bonded to the carbon atom at the 2- or 3-position of thiophene. In the thiophene derivative, the substituent may be bonded to the carbon atom at the 4- or 5-position. When the thiophene derivative is applied, as the substituent bonded to the thiophene ring, there can be cited the above-described substituted or unsubstituted alkyl group, substituted or unsubstituted alkenyl group, substituted or unsubstituted alkynyl group, or the like. Moreover, the halogen such as F or Cl may be substituted for a part of the substituent. These are not restrictive. As the organic substance containing sulfur, thiophene having the thiophene ring or a derivative thereof is preferably used.

[0021] The above-described organic substance containing S is easy to absorb or bond on the metal catalyst with S interposed therebetween. The steric hindrance and water repellency of the organic substance present on the metal catalyst suppress approach of a water molecule to a surface of the metal catalyst, which allows suppression of production of hydrogen due to water decomposition which is a side reaction. Moreover, approach of impurity metal elements dissolved in water is restrained at the same time, and hence the advantage of restraining poisoning on the surface of the catalysis, or the like can be obtained. Depending on a kind and a structure of the catalyst to which the organic substance is imparted, and a required property, it is possible to select one of or a plurality of the above-described organic substances.

[0022] In such an organic substance containing sulfur (S) as described above, a metal (M)-sulfur (S) bond is formed between a sulfur element (S) contained therein and a metal element (M) in the metal catalyst. Sulfur has a property of being easily bonded to a surface of the metal element, which allows enhancement of a bonding property of the organic substance (water-repellent organic substance) to the catalytic metal. This allows the water repellency to be imparted to the surface of the catalytic metal as detailed later. Accordingly, it becomes possible to suppress a decrease in a function as the reduction catalyst of CO_2 due to the approach of water (H_2O) to the surface of the catalytic metal, concretely a

decrease in production efficiency of the carbon compound such as CO due to the catalytic metal, or the like. In the M-S bond, these may be in a chemically bonded state, or may be absorbed by Van der Waals force, absorbed accompanying a chemical reaction between the elements, or the like, for example, and the bonding state is not particularly limited.

[0023] In the catalyst layer 3 including the organic substance and the metal catalyst in which the above-described M-S bond occurs between the sulfur element (S) and the metal element (M), a mass ratio (S/M ratio) of the sulfur element (S) to the metal element (M) in the metal catalyst is set to not less than 0.03 nor more than 0.1. The S/M mass ratio is further preferably not less than 0.05 nor more than 0.09. When the S/M mass ratio is less than 0.03, an insufficient amount of the organic substance with which the surface of the catalytic metal is coated facilitates the approach of the water molecule to a surface of the catalyst layer 3, resulting in a decrease in water repellency. When the S/M mass ratio is more than 0.1, coating with a solid electrolyte component mixed in forming the catalyst layer 3 is not performed effectively, which makes it difficult to form a three-phase boundary, resulting in a possibility of a decrease in ability of the metal catalyst.

[0024] The above-described organic substance containing the sulfur element (S) is preferably contained in a range of not less than 5 mass% nor more than 25 mass%, and further preferably contained in a range of not less than 6 mass% nor more than 20 mass%, relative to a total mass of the carbon material as the support, the metal catalyst, and the water-repellent organic substance. When a content of the organic substance containing S is less than 5 mass%, there is a possibility of insufficient appearance of the water repellency and the steric hindrance caused by the organic substance. When it is more than 25 mass%, there is a possibility of inhibiting a reaction gas from reaching the metal catalyst. Further, a mass ratio of the organic substance containing S to the metal catalyst is preferably not less than 0.3 nor more than 0.9. When the above-described mass ratio is less than 0.3, there is a possibility of permitting the approach of the water molecule to the surface of the metal catalyst. When the above-described mass ratio is more than 0.9, there is a possibility of inhibiting the reaction gas from reaching the metal catalyst, similarly to the above.

[0025] The S/M mass ratio in the catalyst layer 3 is found through the following procedure. Regarding the S element, the quantity can be determined by using, for catalyst powder, for example, a high-frequency induction heating furnace combustion-infrared absorption device (manufactured by HORIBA, Ltd., EMIA-920V2 (trade name)) or a device equal thereto. Regarding the catalytic metal (M), for example, the powder can be dissolved by a pressurized acid leaching method or the like to determine the quantity by using an ICP emission spectrometer (manufactured by Hitachi High-Tech Science Corporation, SPS-3520UVDD (trade name)) or a device equal thereto. The S/M mass ratio is calculated from these measured values.

[0026] The reason why the presence of the above-described water-repellent organic substance containing S on the surface of the catalytic metal allows the production efficiency of the carbon compound (CO or the like) when the CO_2 electrolytic cell is operated for a long time to be maintained effectively is considered as follows. In the cathode catalyst layer 3, moisture resulting from an electrolytic solution and humidification makes it easy that water stays in the layer. This causes an inhibition of diffusion of a CO_2 gas. Moreover, an electrolytic solution component easily moves into the layer together with the water, thus solidifying the electrolytic solution component to cause salt clogging. To achieve stable long-time operation, for the sake of suppressing the movement and the stay of water, it is important to control and maintain the water repellency in the catalyst layer 3.

[0027] To impart the water repellency on the surface of the catalytic metal, after compounding the water-repellent organic substance having S easy to absorb and bond to a surface of metal, it has been found that when the surface of the catalytic metal is coated uniformly with the water-repellent organic substance having S, and the S/M mass ratio of the catalyst layer 3 is not less than 0.03 nor more than 0.1, the approach of water to the surface of the catalytic metal can be effectively suppressed. Further, the presence of the water-repellent organic substance on the surface of the metal allows the solid electrolyte component mixed in forming the catalyst layer 3 to obtain a structure advantageous to formation of the three-phase boundary without covering the surface of the catalytic metal too much. It has been found from these that the cathode catalyst layer 3 suitable for the long-time operation can be obtained. Moreover, carbon fibers are mixed into the catalyst layer 3, thereby obtaining the effect of controlling the water stay in the cathode catalyst layer 3 and suppressing a rise in cell voltage, which is effective in the long-time operation.

[0028] The catalyst layer 3 may include an ion-conductive material or the carbon fiber in addition to the above-described composing materials. The ion-conductive material included in the catalyst layer 3 exhibits an action of transferring ions between the metal catalyst included in the layer and the ion-conductive material. This causes the ion-conductive material to be present in the catalyst layer 3 in a form of coating a part of the metal catalyst. As such an ion-conductive material, a cation exchange resin or an anion exchange resin is preferably used. These are polymers having ionic modifying groups and, for example, a cationic polymer having a perfluorosulfonic acid group is known. More specifically, a cation exchange resin such as Nafion (trade name, manufactured by Du Pont) or Flemion (trade name, manufactured by AGC Inc.,) or an anion exchange resin such as DIAION (trade name, manufactured by Mitsubishi Chemical Corporation) can be used. A content of the ion-conductive material is preferably not less than 0.1 times nor more than 1 time, and more preferably not less than 0.1 times nor more than 0.8 times, relative to the total mass of the above-described carbon material and metal catalyst. When the content of the ion-conductive material is less than 0.1 times relative to the total

mass of the carbon material and the metal catalyst, it becomes difficult to maintain a structure of the catalyst layer 3 during the long-time operation, resulting in a decrease in the production efficiency of the carbon compound. Further, when it is more than 1 time, filling pores in the catalyst layer 3 with the ion-conductive material rapidly increases the cell voltage. A volume of the ion-conductive material is preferably not less than 0.1 times nor more than 1.5 times, and more preferably not less than 0.16 times nor more than 1.2 times, relative to the total volume of the above-described carbon material and metal catalyst. When the volume of the ion-conductive material is less than 0.1 times relative to the total volume of the carbon material and the metal catalyst, it becomes difficult to maintain the structure of the catalyst layer 3 during the long-time operation, resulting in a decrease in the production efficiency of the carbon compound. Further, when it is more than 1.5 times, filling the pores in the catalyst layer 3 with the ion-conductive material rapidly increases the cell voltage.

[0029] The carbon fiber mixed into the catalyst layer 3 may be in a tube shape or in a fiber shape, and has an average diameter, preferably of not less than 10 nm nor more than 100 nm, and further preferably of not less than 30 nm nor more than 100 nm. By using the carbon fiber having the average diameter in the above-described range, the pores are formed effectively in the catalyst layer 3. An average length of the carbon fiber is preferably not less than 5 μm nor more than 100 μm. The average length of less than 5 μm makes it difficult to form the pores in the catalyst layer 3, resulting in also being less effective in a decrease in the cell voltage. The average length of more than 100 μm does not allow uniform coating with the forming material of the catalyst layer 3, resulting in impairing thickness uniformity in the surface. A mass ratio of the carbon fiber in the catalyst layer 3 is preferably not less than 10 mass% nor more than 70 mass%, and further preferably not less than 30 mass% nor more than 60 mass%. When the mass ratio of the carbon fiber is less than 10 mass%, a pore effective in gas diffusion is difficult to obtain. When the mass ratio of the carbon fiber exceeds 70 mass%, a decrease in density of the metal catalyst decreases the production efficiency of the carbon compound. The average diameter and the average length of the carbon fibers are measured as follows. The five fields of SEM images which diameters of ten or more of the carbon fibers enter are randomly selected. The diameters of arbitrary ten fibers in each field are measured, and the mean of the measurements in each field is calculated. Further, the means of the five fields are averaged, and such a mean value is assumed the average diameter of the carbon fiber. The five fields of SEM images which lengths of ten or more of the carbon fibers enter are randomly selected. The lengths of arbitrary ten fibers in each field are measured, and the mean of the measurements in each field is calculated. Further, the means of the five fields are averaged, and such a mean value is assumed the average length of the carbon fiber.

[0030] Next, the carbon dioxide electrolytic device of the embodiment will be described with reference to FIG. 2 and FIG. 3. FIG. 2 is a sectional view illustrating a carbon dioxide (CO_2) electrolytic device 10 of the embodiment using the above-described reduction electrode. The CO_2 electrolytic device 10 illustrated in FIG. 2 includes an electrolytic cell 20. The electrolytic cell 20 includes a cathode part 30, an anode part 40, and a separator 50 disposed to separate these.

[0031] The cathode part 30 includes a reduction electrode (cathode) 31 having the catalyst layer of the embodiment, a gas flow path 32, and a cathode current collector 33. The gas flow path 32 is a flow path which supplies a CO_2 gas to the cathode 31, and is formed of a pit (groove) provided in a first flow path plate 34. The cathode 31 is disposed to be in contact with CO_2 flowing through the gas flow path 32. The anode part 40 includes an anode (oxidation electrode) 41, an anode solution flow path 42, and an anode current collector 43. The anode solution flow path 42 is a flow path which supplies an anode solution to the anode 41, and is formed of a pit (groove) provided in a second flow path plate 44. The anode 41 is disposed to be in contact with the anode solution flowing through the anode solution flow path 42.

[0032] The CO_2 electrolytic device 10 includes a gas supply part 60 which supplies CO_2 to the electrolytic cell 20, and an anode solution supply part 70 which supplies the anode solution to the electrolytic cell 20. The gas supply part 60 includes a CO_2 storage 61 such as a CO_2 gas cylinder and a gas flow rate control unit 62, and the CO_2 gas is supplied from the CO_2 storage 61 via the gas flow rate control unit 62 and a gas pipe 63 to the gas flow path 32. The CO_2 gas supplied to the gas flow path 32 is not limited to a single gas of CO_2, and only needs to be a gas mainly composed of CO_2 (for example, a gas containing CO_2 of 90 vol% or more). The anode solution supply part 70 includes an anode solution tank 71, a pump 72, and a flow rate control unit 73, and the anode solution is supplied from the anode solution tank 71 via the pump 72, the flow rate control unit 73, and a solution pipe 74 to the anode solution flow path 42. The anode solution circulates through the anode solution flow path 42 and the solution pipe 74. The cathode 31 and the anode 41 in the CO_2 electrolytic device 10 are connected to a power supply 80.

[0033] The cathode part 30 in the electrolytic cell 20 may have a cathode solution flow path 35, as illustrated in FIG. 3. The cathode solution flow path 35 is formed of a pit (recessed portion) provided in a third flow path plate 36. The cathode part 30 illustrated in FIG. 3 is formed by stacking the third flow path plate 36 forming the cathode solution flow path 35, the cathode 31, the first flow path plate 34 forming the gas flow path 32, and the cathode current collector 33 in order. Such a CO_2 electrolytic device 10 includes a cathode solution supply part 90 which supplies a cathode solution to the electrolytic cell 20. The cathode solution supply part 90 includes a cathode solution tank 91, a pump 92, and a flow rate control unit 93, and the cathode solution is supplied from the cathode solution tank 91 via the pump 92, the flow rate control unit 93, and a solution pipe 94 to the cathode solution flow path 35. The cathode solution circulates through the cathode solution flow path 35 and the solution pipe 94.

[0034] In the cathode 31 of the electrolytic cell 20 illustrated in FIG. 2, the anode solution and ions are supplied through the separator 50, and the CO_2 gas is supplied from the gas flow path 32. A CO_2 reduction product is discharged mainly from the gas flow path 32. In the cathode 31 of the electrolytic cell 20 illustrated in FIG. 3, the cathode solution and ions are supplied from the cathode solution flow path 35, and the CO_2 gas is supplied from the gas flow path 32. A gaseous CO_2 reduction product is discharged mainly from the gas flow path 32, and a liquid CO_2 reduction product is discharged mainly from the cathode solution flow path 35. Therefore, the electrolytic cell 20 illustrated FIG. 3 is preferably used when a liquid carbon compound such as formic acid (HCOOH), methanol (CH_3OH), ethanol (C_2H_5OH), formaldehyde (HCHO), or ethylene glycol ($C_2H_6O_2$) is produced. These products are dissolved in the cathode solution, thereby facilitating recovery.

[0035] For the flow path plate 44 forming the anode solution flow path 42, and the flow path plate 34 forming the gas flow path 32, a material having low chemical reactivity and having high conductivity is preferably used. As such a material, there can be cited a metal material such as Ti or SUS, carbon, or the like. For the flow path plate 36 forming the cathode solution flow path 35, 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.

[0036] The electrolytic cell 20 is, in general, sandwiched by a pair of support plates (not illustrated), and further tightened by bolts or the like. In FIG. 2 and FIG. 3, a reference sign 80 denotes a power supply which passes current through the anode 41 and the cathode 31. The power supply 80 is not limited to an ordinary commercial power supply, a battery, or the like, and may be a power supply which converts renewable energy into electric energy and supplies it. As examples of such a power supply, there can be cited a power supply which converts kinetic energy or potential energy such as wind power, water power, geothermal power or tidal power into electric energy, a power supply such as a solar cell having a photoelectric conversion element which converts light energy into electric energy, a power supply such as a fuel cell or a storage battery which converts chemical energy into electric energy, and a power supply such as a device which converts vibrational energy such as sound into electric energy. The use of renewable energy is also combined with effective use of carbon dioxide to be preferable in terms of the environment.

[0037] The anode 41 is an electrode (oxidation electrode) which causes an oxidation reaction of water (H_2O) in the anode solution to produce oxygen (O_2) and hydrogen ions (H^+), or causes an oxidation reaction of hydroxide ions (OH^-) produced in the cathode part 30 to produce oxygen and water. The anode 41 is disposed between the separator 50 and the anode solution flow path 42 to be in contact with them. In more detail, the anode 41 has a first surface in contact with the separator 50 and a second surface facing the anode solution flow path 42. The first surface of the anode 41 is in close contact with the separator 50. A solution inlet port and a solution outlet port (both of which are not illustrated) are connected with the second flow path plate 44, and via these solution inlet port and solution outlet port, the anode solution is introduced and discharged by the pump 72. The anode solution flows through in the anode solution flow path 42 so as to be brought into contact with the anode 41. The anode current collector 43 is in electrical contact with a surface on an opposite side to the anode 41 on the second flow path plate 44 forming the anode solution flow path 42.

[0038] The compound produced by the oxidation reaction on the anode 41 is different depending on a kind of an oxidation catalyst, or the like. When an aqueous electrolyte solution is used, the anode 41 is preferably composed mainly of a catalyst material (anode catalyst material) capable of oxidizing water (H_2O) to produce oxygen and hydrogen ions or oxidizing hydroxide ions (OH^-) to produce water and oxygen, and capable of reducing an overvoltage in the above reaction. As such a catalyst material, there can be cited a metal such as platinum (Pt), palladium (Pd), or nickel (Ni), an alloy or an intermetallic compound containing the above metal, a binary metal oxide such as a manganese oxide (Mn-O), an iridium oxide (Ir-O), a nickel oxide (Ni-O), a cobalt oxide (Co-O), an iron oxide (Fe-O), a tin oxide (Sn-O), an indium oxide (In-O), a ruthenium oxide (Ru-O), a lithium oxide (Li-O), or a lanthanum oxide (La-O), a ternary metal oxide such as Ni-Co-O, Ni-Fe-O, La-Co-O, Ni-La-O, or Sr-Fe-O, a quaternary metal oxide such as Pb-Ru-Ir-O or La-Sr-Co-O, or a metal complex such as a Ru complex or an Fe complex.

[0039] The anode 41 preferably includes a base material having a structure capable of moving the anode solution and ions between the separator 50 and the solution flow path 42, for example, a porous structure such as a mesh material, a punched material, or a porous body. As the base material having the porous structure, the one having relatively large pores such as a metal fiber sintered compact is also included. The base material may be composed 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 the metals, or may be composed of the above-described anode catalyst material. When the oxide is used as the anode catalyst material, it is preferable to form a catalyst layer by attaching or staking the anode catalyst material on the surface of the base material composed of the above-described metal material. The anode catalyst material preferably has a shape of a nanoparticle, a nanostructure, a nanowire or the like in order to enhance the oxidation reaction. The nanostructure is a structure obtained by forming nanoscale irregularities on the surface of the catalyst material. Further, the anode (oxidation electrode) 41 need not always be provided with the oxidation catalyst. An oxidation catalyst layer provided other than the oxidation electrode may be electrically connected to the oxidation electrode.

[0040] As each of the anode solution and the cathode solution, an aqueous solution containing an optional electrolyte

can be used. As the aqueous solution containing the electrolyte, there can be cited, for example, an aqueous solution containing a phosphate ion (PO_4^{2-}), a borate ion (BO_3^{3-}), a sodium ion (Na^+), a potassium ion (K^+), a calcium ion (Ca^{2+}), a lithium ion (Li^+), a cesium ion (C_S^+), a magnesium ion (Mg^{2+}), a chloride ion (Cl^-), a hydrogen carbonate ion (HCO_3^-), a carbonate ion (CO_3^{2-}), or the like. In addition, an aqueous solution containing $LiHCO_3$, $NaHCO_3$, $KHCO_3$, C_SHCO_3, a phosphoric acid, or the like may be used.

[0041] 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 BF4 or 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 amine 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.

[0042] The separator 50 is formed of an ion exchange membrane or the like capable of moving ions between the anode 41 and the cathode 31, and capable of separating the anode part 40 and the cathode part 30. As the ion exchange membrane, there can be cited, for example, a cation exchange membrane such as Nafion (registered trademark) or Flemion (registered trademark), or an anion exchange membrane such as Neosepta (registered trademark), Selemion (registered trademark), or Sustainion (registered trademark). Further, when the movement of ions need not be controlled between the two electrolytic solutions, the ion exchange membrane need not always be provided in the electrolytic cell 20. For the separator 50, other than the ion exchange membrane, a glass filter or a filler filled with agar or the like, an insulating porous body such as zeolite or an oxide, or a polymer membrane capable of passing water molecules and ions therethrough may be used as long as they are each a material capable of moving ions between the anode and the cathode. However, the circulation of gas between the cathode part 30 and anode part 40 sometimes causes a circular reaction due to reoxidation of the reduction product. Therefore, it is more preferable to reduce the gas exchange between the cathode part 30 and the anode part 40.

[0043] The supplied CO_2 gas may be supplied in a dry state, but is more preferably humidified. This allows prevention of drying of the membrane when the ion exchange membrane is used for the separator 50. A CO_2 concentration of the supplied gas need not be 100%. Despite a decrease in efficiency, it is also possible to reduce gases containing carbon dioxide emitted in various facilities.

[0044] Next, an operation example of the carbon dioxide electrolytic device 10 illustrated in FIG. 2 will be described. Here, a case of producing carbon monoxide (CO) as the carbon compound is mainly described. However, the carbon compound as the reduction product of carbon dioxide is not limited to carbon monoxide, and may be methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), methanol (CH_3OH), ethanol (C_2H_5OH), ethylene glycol ($C_2H_6O_2$), or the like, and moreover, carbon monoxide which is a reduction product may be further reduced to produce such organic compounds as described above. When the carbon compound in a solution form is produced as described above, the electrolytic cell 20 illustrated in FIG. 3 is preferably used. Further, a reaction process caused by the electrolytic cell 20 is considered to be the main production of hydrogen ions (H^+) and the main production of hydroxide ions (OH^-), but is not limited to either of these reaction processes.

[0045] First, the reaction process when water (H_2O) is oxidized mainly to produce hydrogen ions (H^+) is described. When current is supplied from the power supply 80 between the anode 41 and the cathode 31, an oxidation reaction of water (H_2O) occurs in the anode 41 with which the anode solution is brought into contact. Concretely, as presented in the following formula (1), H_2O contained in the anode solution is oxidized, and oxygen (O_2) and hydrogen ions (H^+) are produced.

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

[0046] H^+ produced in the anode moves in the electrolytic solution present in the anode 41 and the separator 50, and reaches the vicinity of the cathode 31. The reduction reaction of carbon dioxide (CO_2) is caused by electrons (e^-) based on the current supplied from the power supply 80 to the cathode 31 and H^+ moved to the vicinity of the cathode 31. Concretely, as presented in the following formula (2), CO_2 supplied from the CO_2 gas flow path 32 to the cathode 31 is reduced to produce CO. Further, as presented in the following formula (3), hydrogen ions (H^+) receive electrons, thereby producing hydrogen. Hydrogen may be produced simultaneously with the production of carbon monoxide.

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

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

[0047] Next, the reaction process when carbon dioxide (CO_2) is reduced mainly to produce hydroxide ions (OH^-) is described. When current is supplied from the power supply 80 between the anode 41 and the cathode 31, in the vicinity of the cathode 31, as presented in the following formula (4), water (H_2O) and carbon dioxide (CO_2) are reduced to produce carbon monoxide (CO) and hydroxide ions (OH^-). Further, as presented in the following formula (5), water receives electrons, thereby producing hydrogen. At this time, hydrogen may be produced simultaneously with the pro-

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

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

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

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

[0048] Such a carbon dioxide electrolytic device of the embodiment is not only specialized in only the reduction of carbon dioxide, but also, for example, can produce carbon monoxide and hydrogen at 1:2, and produce a carbon dioxide reduction product and hydrogen at such an optional ratio as to produce methanol in a chemical reaction thereafter. Hydrogen is a material which is inexpensive and easy to obtain through the electrolysis of water and from fossil fuel, and hence a ratio of hydrogen is not required to be large. A ratio of carbon monoxide to hydrogen is at least 1 or more, and desirably 1.5 or more from these viewpoints, which is preferable from economical and environmental viewpoints.

[0049] In the above-described carbon dioxide electrolytic device 10 of the embodiment, as the reduction catalyst of the cathode 31, there is applied the previously-described electrode catalyst layer which includes the carbon material, the metal catalyst supported on the carbon material, and the water-repellent organic substance containing S of the embodiment, and in which the mass ratio (S/M) of the sulfur element (S) to the metal element (M) in the metal catalyst is not less than 0.03 nor more than 0.1, thus making it possible to suppress the approach of water to the surface of the catalytic metal, and moreover to obtain the structure advantageous to formation of the three-phase boundary on the surface of the catalytic metal. These increase the production efficiency of the carbon compound such as CO in the carbon dioxide electrolytic device 10, and allow the production efficiency of the carbon compound to be maintained even when the carbon dioxide electrolytic device 10 is operated for a long time.

EXAMPLES

[0050] Next, examples and evaluation results thereof will be described.

(Example 1)

[0051] First, as composing materials of a cathode catalyst layer, catalytic particles in which Au nanoparticles (metal catalyst) each having an average diameter of 2 nm were supported on carbon particles, 2-octylthiophene as a water-repellent organic substance (organic substance containing S), and a Nafion solution (trade name, manufactured by Du Pont) as an ion-conductive material (ion-exchange resin) were prepared. The materials, pure water, and isopropanol were mixed at a predetermined ratio to prepare a catalyst coating solution. The catalytic particles and the water-repellent organic substance were mixed so that a ratio of S in the water-repellent organic substance to a metal element M (Au) in the catalyst layer was 0.08. Nafion as a solid electrolyte was mixed so that its solid mass was 0.23 times relative to a total mass of the support carbon material and the gold catalyst.

[0052] A sheet of carbon paper with a diffusion layer having a microporous layer was prepared as an electrode base material. A spray nozzle was filled with the above-described catalyst coating solution, which was sprayed on the carbon paper disposed on a heated hot plate to perform spray coating. The spray coating of the catalyst coating solution was performed so that a thickness of a cathode was 60 μm. Further, a mass of the metal catalyst per unit area of the catalyst layer was set to 0.2 mg/cm^2. This coated carbon paper was cut into a size of 4 $\times$ 4 cm to serve as the cathode (an electrode area: 16 cm^2).

[0053] As an anode, an electrode in which a Ti mesh was coated thereon with IrO_2 nanoparticles serving as a catalyst was used. This IrO_2/Ti mesh was cut into 4 $\times$ 4 cm to serve as the anode.

[0054] Next, an electrolytic cell illustrated in FIG. 2 was fabricated. A cathode current collector, a CO_2 gas flow path, the cathode, a separator, the anode, an anode solution flow path, and an anode current collector were stacked in that order from the top, sandwiched by non-illustrated support plates, and further tightened by bolts to fabricate the electrolytic cell. For the separator, Sustainion (trade name, manufactured by Dioxide Materials, Inc.) was used as an anion exchange membrane. The anode current collector and the cathode current collector are connected to an external power supply, and a carbon dioxide electrolytic device illustrated in FIG. 2 was fabricated.

(Example 2)

[0055] Except that in the catalyst coating solution in Example 1, the catalytic particles and the water-repellent organic substance were mixed so that a ratio of S in the water-repellent organic substance to the metal element M (catalytic

metal) in the catalyst layer was 0.07, and Nafion was added to the catalyst coating solution as the solid electrolyte so that a mass ratio of the electrolyte/the total mass of the support carbon material and the gold catalyst was 0.51, a catalyst coating solution was prepared in a manner similar to that in Example 1. A cathode was produced in a manner similar to that in Example 1 by using such a catalyst coating solution. Next, except that the cathode in Example 1 was changed into the above-described cathode in Example 2, an electrolytic cell and an electrolytic device illustrated in FIG. 2 were fabricated in a manner similar to those in Example 1.

(Example 3)

[0056] Except that in the catalyst coating solution in Example 1, carbon fibers each having an average diameter of 50 nm and an average length of 10 μm were further mixed so that a ratio of the carbon fiber in a catalyst layer was 30 mass%, and Nafion was added to the catalyst coating solution as the solid electrolyte so that a mass ratio to a total mass of the support carbon material and the gold catalyst was 0.25, a catalyst coating solution was prepared in a manner similar to that in Example 1. A cathode was produced in a manner similar to that in Example 1 by using such a catalyst coating solution. Next, except that the cathode in Example 1 was changed into the above-described cathode in Example 3, an electrolytic cell and an electrolytic device illustrated in FIG. 2 were fabricated in a manner similar to those in Example 1.

[0057] Next, the electrolytic devices in Examples 1 to 3 were each operated under the conditions indicated below. CO_2 was supplied to the CO_2 gas flow path in a predetermined amount, and an aqueous sodium hydrogen carbonate solution (a concentration of 0.1 M) was made to flow through the anode solution flow path. A constant current of 200 mA/cm^2 was continuously applied between the anode and the cathode to perform the long-time operation. At that time, a gas produced from the cathode side was collected to measure conversion efficiency of CO. The gas produced by the aforesaid operation was composed of CO and hydrogen, and the addition of their partial current densities nearly matched the above-described value of the current density. Regarding the electrolytic devices in Examples 1 to 3, FIG. 4 illustrates time changes in production efficiency of CO under the above-described conditions.

(Comparative example 1)

[0058] Except that in the catalyst coating solution in Example 1, no water-repellent organic substance was added, a catalyst coating solution was prepared in a manner similar to that in Example 1. Nafion as the solid electrolyte was mixed into the catalyst coating solution so that a mass ratio to the total mass of the support carbon material and the gold catalyst was 0.20. A cathode was produced in a manner similar to that in Example 1 by using such a catalyst coating solution. Next, except that the cathode in Example 1 was changed into the above-described cathode in Comparative example 1, an electrolytic cell and an electrolytic device illustrated in FIG. 2 were fabricated in a manner similar to those in Example 1.

(Comparative example 2)

[0059] Except that in the catalyst coating solution in Example 1, the catalytic particles and the water-repellent organic substance were mixed so that a ratio of S in the water-repellent organic substance to the metal element M (Au) in the catalyst layer was 0.01, a catalyst coating solution was prepared in a manner similar to that in Example 1. Nafion as the solid electrolyte was added to the catalyst coating solution so that a mass ratio to the total mass of the support carbon material and the gold catalyst was 0.03. A cathode was produced in a manner similar to that in Example 1 by using such a catalyst coating solution. Next, except that the cathode in Example 1 was changed into the above-described cathode in Comparative example 2, an electrolytic cell and an electrolytic device illustrated in FIG. 2 were fabricated in a manner similar to those in Example 1.

[0060] The electrolytic devices in Comparative examples 1 to 2 were each subjected to an operation test under the same conditions as those in Example 1. Regarding the electrolytic devices in Comparative examples 1 to 2, FIG. 4 illustrates time changes in production efficiency of CO under the above-described conditions. Further, Table 1 presents production conditions of the cathode catalyst layers in the examples and the comparative examples.

[Table 1]

	S/metal catalyst (Au) (mass ratio)	Electrolyte/total mass of carbon material and gold catalyst (mass ratio)	Carbon fiber
Example 1	0.08	0.23	Absence
Example 2	0.07	0.51	Absence
Example 3	0.08	0.25	Presence

(continued)

	S/metal catalyst (Au) (mass ratio)	Electrolyte/total mass of carbon material and gold catalyst (mass ratio)	Carbon fiber
Comparative example 1	0	0.20	Absence
Comparative example 2	0.01	0.03	Absence

[0061] As is obvious from FIG. 4, it is found that the electrolytic devices in Examples 1 to 3 have the catalyst layers suitable for the long-time operation without observing a decrease in production efficiency of CO even in performing the long-time operation. On the other hand, as in Comparative example 1, in the electrolytic device using the catalyst layer containing no sulfur, the production efficiency of CO at the initial stage was low, and a rapid decrease in the efficiency with elapse of operation time was observed. Further, as in Comparative example 2, when the ratio of S in the water-repellent organic substance to the metal element M (catalytic metal) was low (less than 0.03), the production efficiency of CO at the initial stage was equal to those in Examples 1 to 3, but a decrease in the efficiency was noticeable with elapse of time. Note that an electrolytic device using a catalyst layer in which a mass ratio of S/metal catalyst (Au) was set to a value exceeding 0.1 failed to obtain sufficient production efficiency of CO. Further, when a mass ratio of the electrolyte/a total mass of the support carbon material and the gold catalyst was too low, the production efficiency of CO also decreased with elapse of time, similarly to Comparative example 2. In an electrolytic device using a catalyst layer in which a mass ratio of the electrolyte/the total mass of the support carbon material and the gold catalyst was set to 2, too high a cell voltage did not allow the measurement.

[0062] Note that configurations of the embodiments may be each applied in combination, and further may be partially substituted. Herein, while certain embodiments of the present 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.

Claims

1. An electrode catalyst layer for electrolytic cell of carbon dioxide, the electrode catalyst layer comprising: a carbon material; a metal catalyst supported on the carbon material; and a water-repellent organic substance, wherein

   the water-repellent organic substance includes an organic substance containing sulfur,
   the organic substance containing sulfur has a metal-sulfur bond formed between the sulfur and the metal catalyst, and
   a mass ratio of a sulfur element to a metal element in the metal catalyst in the catalyst layer is 0.03 or more and 0.1 or less.

2. The electrode catalyst layer according to claim 1, wherein the organic substance containing sulfur is contained in a range of 5 mass% or more and 25 mass% or less to a total mass of the carbon material, the metal catalyst, and the water-repellent organic substance.

3. The electrode catalyst layer according to claim 1 or claim 2, wherein a mass ratio of the organic substance containing sulfur to the metal catalyst is 0.3 or more and 0.9 or less.

4. The electrode catalyst layer according to any one of claim 1 to claim 3, further comprising an ion-conductive material, wherein a solid mass of the ion-conductive material is 0.1 times or more and 1 time or less to a total mass of the carbon material and the metal catalyst.

5. The electrode catalyst layer according to any one of claim 1 to claim 4, further comprising a carbon fiber having an average diameter of 10 nm or more and 100 nm or less and an average length of 5 μm or more and 100 μm or less, wherein a ratio of the carbon fiber in the catalyst layer is 10 mass% or more and 70 mass% or less.

6. The electrode catalyst layer according to any one of claim 1 to claim 5, wherein the organic substance containing sulfur has a thiophene ring.

7. The electrode catalyst layer according to any one of claim 1 to claim 6, wherein a thickness of the catalyst layer is 5 μm or more and 200 μm or less.

8. The electrode catalyst layer according to any one of claim 1 to claim 7, wherein the carbon material includes at least one selected from the group consisting of a carbon particle, a carbon nanotube, activated carbon, and graphene.

9. The electrode catalyst layer according to any one of claim 1 to claim 8,

wherein the metal catalyst includes at least one metal selected from the group consisting of gold, silver, copper, platinum, palladium, nickel, cobalt, iron, manganese, titanium, cadmium, zinc, indium, gallium, lead, and tin, an alloy containing the metal, or an oxide of the metal, and
wherein the metal catalyst has at least one structure selected from the group consisting of a nanoparticle, a nanostructure, and a nanowire.

10. The electrode catalyst layer according to any one of claim 1 to claim 9, wherein a mass of the metal catalyst per unit area of the catalyst layer is 0.01 mg/cm^2 or more and 5 mg/cm^2 or less.

11. The electrode catalyst layer according to claim 4, wherein the ion-conductive material includes a cation exchange resin or an anion exchange resin.

12. An electrode for electrolytic cell comprising:

a conductive base material; and
the electrode catalyst layer according to any one of claim 1 to claim 11, provided on the conductive base material.

13. The electrode according to claim 12, wherein the conductive base material includes a material containing at least one selected from the group consisting of titanium, nickel, iron, and carbon.

14. The electrode according to claim 12 or claim 13, wherein the conductive base material has at least one selected from the group consisting of a mesh material, a punched material, a porous body, and a metal fiber sintered compact.

15. A carbon dioxide electrolytic device comprising:

an electrolytic cell including a cathode part having a cathode constituted of the electrode according to any one of claim 12 to claim 14, which is disposed to be in contact with carbon dioxide and reduces the carbon dioxide to produce a carbon compound, and a gas flow path to supply carbon dioxide to the cathode, an anode part having an anode disposed to be in contact with an anode solution containing water or a hydroxide ion and oxidize the water or the hydroxide ion to produce oxygen, and an anode solution flow path to supply the anode solution to the anode, and a separator separating the cathode part and the anode part;
a gas supply part to supply carbon dioxide to the gas flow path; and
a solution supply part to supply the anode solution to the anode solution flow path,
wherein the cathode and the anode are configured to be supplied with current from a power supply.

FIG. 1

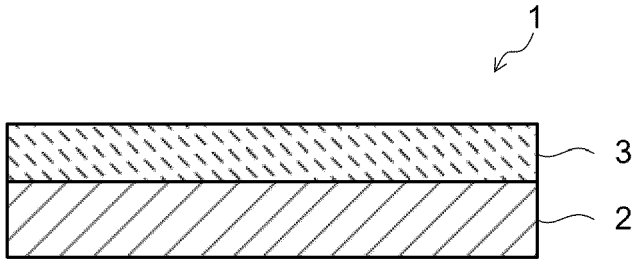

FIG. 2

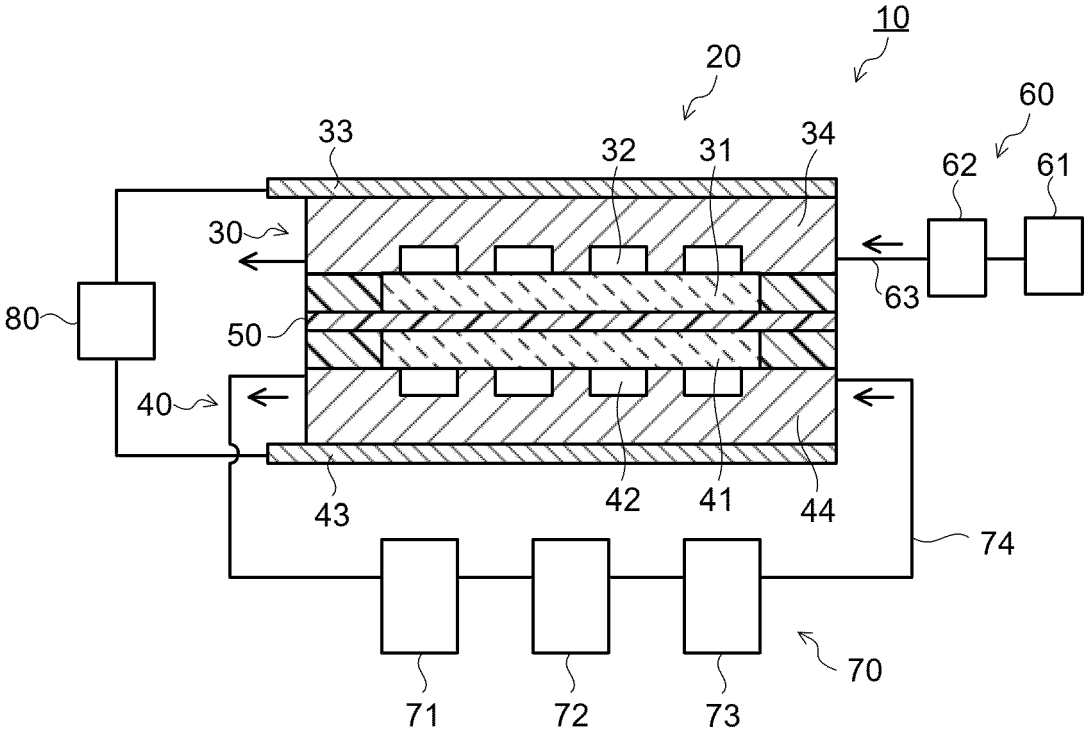

FIG. 3

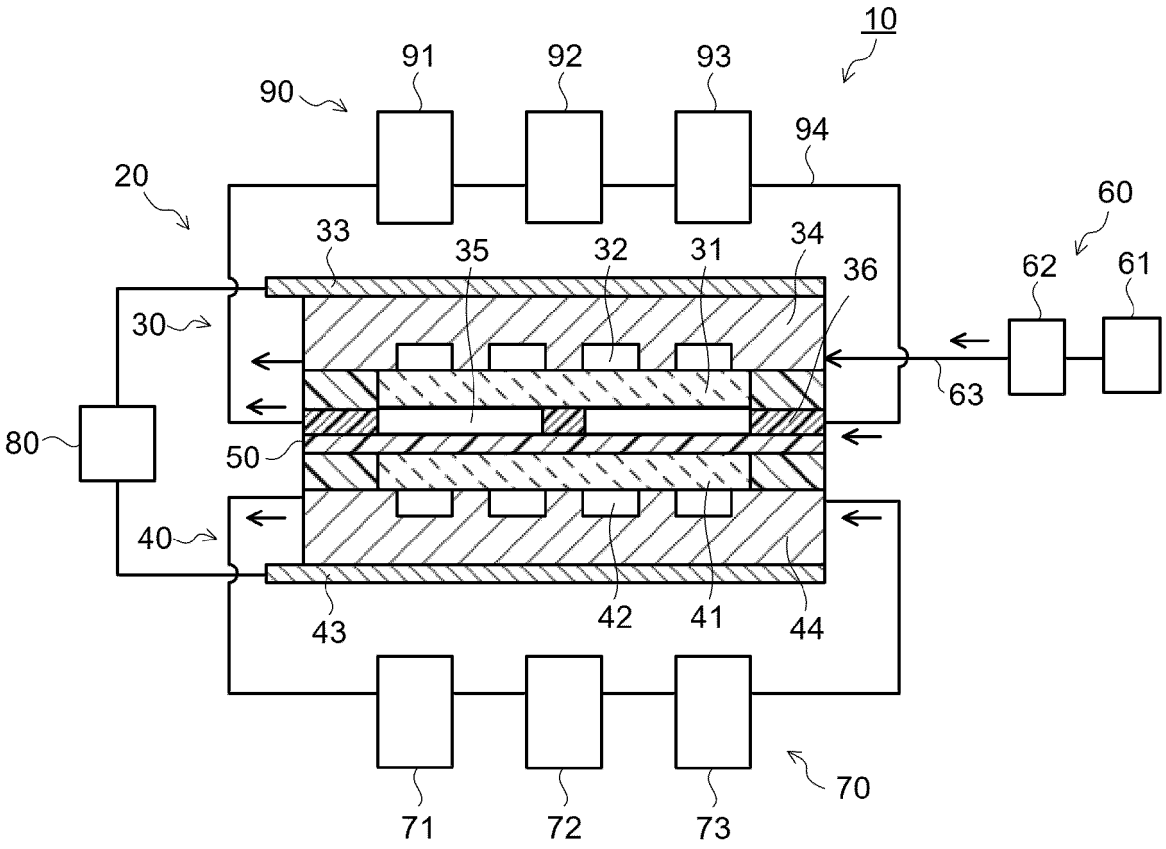
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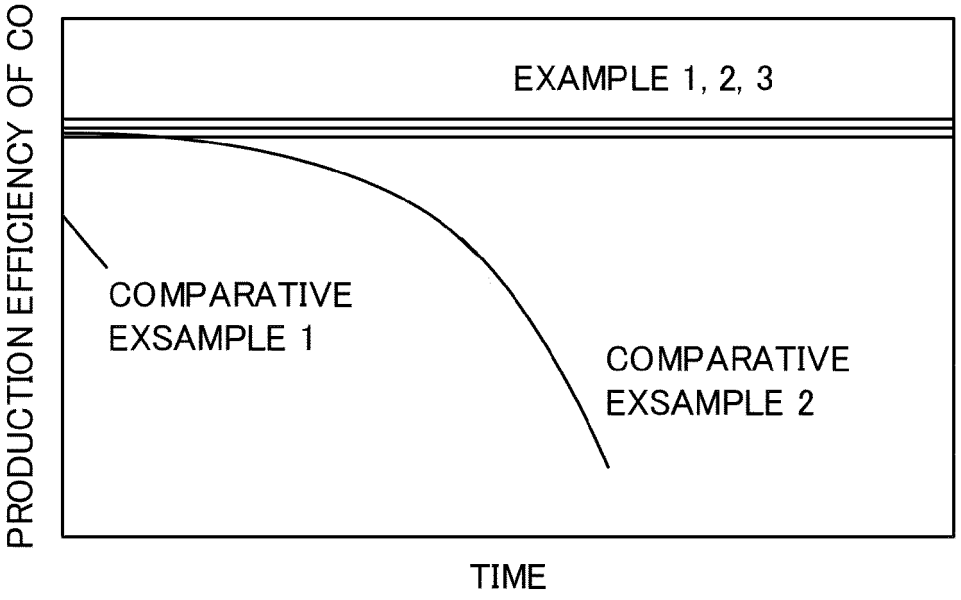
FIG. 4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EUROPEAN SEARCH REPORT

Application Number
EP 22 19 3142

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	US 2021/164117 A1 (FUJINUMA NAOHIRO [US]) 3 June 2021 (2021-06-03) * the whole document *	1-15	INV. C25B9/19 C25B11/065 C25B11/052 C25B11/054 C25B11/069
A	US 2020/347502 A1 (DISMUKES G CHARLES [US] ET AL) 5 November 2020 (2020-11-05) * the whole document *	1-15	
A	US 2020/216968 A1 (HUNEGNAW SARA [US] ET AL) 9 July 2020 (2020-07-09) * the whole document *	1-15	
A	JP 2000 144466 A (PERMELEC ELECTRODE LTD) 26 May 2000 (2000-05-26) * the whole document *	1-14	

TECHNICAL FIELDS SEARCHED (IPC)

C25B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	14 August 2023	Juhart, Matjaz

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14-08-2023

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2021164117 A1	03-06-2021	CN 111032920 A	17-04-2020
		EP 3690081 A1	05-08-2020
		JP 7235666 B2	08-03-2023
		JP WO2019065258 A1	05-11-2020
		US 2021164117 A1	03-06-2021
		WO 2019065258 A1	04-04-2019
US 2020347502 A1	05-11-2020	NONE	
US 2020216968 A1	09-07-2020	AU 2020206328 A1	05-08-2021
		CA 3125442 A1	16-07-2020
		CN 113646468 A	12-11-2021
		EP 3908685 A1	17-11-2021
		JP 2022516277 A	25-02-2022
		KR 20210132024 A	03-11-2021
		US 2020216968 A1	09-07-2020
		WO 2020146402 A1	16-07-2020
JP 2000144466 A	26-05-2000	JP 3949299 B2	25-07-2007
		JP 2000144466 A	26-05-2000

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