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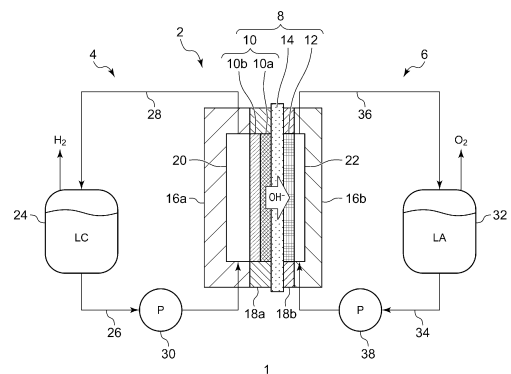
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(54) **APPARATUS FOR PRODUCING ORGANIC HYDRIDE AND METHOD FOR PRODUCING ORGANIC HYDRIDE**

(57) An apparatus (2) for producing an organic hydride includes: a cathode electrode (10) that generates an organic hydride and hydroxide ions from a substance to be hydrogenated and water; an anode electrode (12) that generates oxygen by oxidizing the hydroxide ions; and an electrolyte membrane (14) that is composed of an anion exchange membrane and is arranged between the cathode electrode (10) and the anode electrode (12) so as to transfer the hydroxide ions from the cathode electrode (10) side to the anode electrode (12) side.

FIG. 1



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Description

TECHNICAL FIELD

- 5 **[0001]** The present invention relates to an apparatus for producing an organic hydride and a method for producing an organic hydride.

BACKGROUND ART

- 10 **[0002]** In recent years, in order to suppress the carbon dioxide emission amount in the energy generation process, renewable energy is expected to be used, which is obtained by solar light, wind power, hydraulic power, geothermal power generation, and the like. As an example, a system for generating hydrogen by performing water electrolysis using power derived from renewable energy has been devised. In addition, an organic hydride system has attracted attention as an energy carrier for large-scale transportation and storage of hydrogen derived from renewable energy.
- 15 **[0003]** Regarding the technology for producing an organic hydride, there has been known an apparatus for producing an organic hydride having an anode electrode that generates protons from water, a cathode electrode that hydrogenates an organic compound having an unsaturated bond (a substance to be hydrogenated), and an electrolyte membrane that separates the anode electrode and the cathode electrode (see, for example, Patent Literature 1). In this apparatus for producing an organic hydride, protons are generated by oxidation of water at the anode electrode, these protons then
- 20 move to the cathode electrode side via the electrolyte membrane, and a substance to be hydrogenated is hydrogenated by the protons at the cathode electrode, thereby producing an organic hydride.

RELATED-ART LITERATURE

- 25 PATENT LITERATURE

[0004] Patent Literature 1: WO 2012/091128

SUMMARY OF INVENTION

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TECHNICAL PROBLEM

- [0005]** In the above-described apparatus for producing an organic hydride, the protons bind with water in the anode chamber so as to become oxonium ions and then move to the cathode electrode side via the electrolyte membrane. When
- 35 three elements: oxonium ions, a substance to be hydrogenated; and electrons, are present in the reaction field of the cathode electrode, the protons are consumed from the oxonium ions, and a hydrogenation reaction of the substance to be hydrogenated occurs. As a result of this, water is produced. Further, as the ions move, the water solvated with the protons also moves at the same time. Hereinafter, water that moves through the electrolyte membrane with the movement of ions is collectively referred to as "electroosmotic water." If electroosmotic water accumulates on the cathode electrode side, it
- 40 may hinder the hydrogenation of the substance to be hydrogenated or may require a lot of work to separate the water from the organic hydride. As a result, the production efficiency of the organic hydride can be reduced.

[0006] The present invention has been made in view of such a situation, and an object thereof is to provide a technique for improving the production efficiency of organic hydrides.

- 45 SOLUTION TO PROBLEM

- [0007]** One embodiment of the present invention relates to an apparatus for producing an organic hydride. This apparatus for producing an organic hydride includes: a cathode electrode that generates an organic hydride and hydroxide ions from a substance to be hydrogenated and water; an anode electrode that generates oxygen by oxidizing the hydroxide
- 50 ions; and an electrolyte membrane that is composed of an anion exchange membrane and is arranged between the cathode electrode and the anode electrode so as to transfer the hydroxide ions from the cathode electrode side to the anode electrode side.

- [0008]** Another embodiment of the present invention relates to a method for producing an organic hydride in which the apparatus for producing an organic hydride according to the above embodiment is used. The method for producing an organic hydride includes: producing an organic hydride and hydroxide ions from the substance to be hydrogenated and water at the cathode electrode; moving the hydroxide ions to the anode electrode via the electrolyte membrane; and producing oxygen by oxidizing the hydroxide ions at the anode electrode.

[0009] Optional combinations of the aforementioned constituting elements, and implementations of the present

disclosure in the form of methods, apparatuses, and systems may also be practiced as additional modes of the present disclosure.

ADVANTAGEOUS EFFECTS OF INVENTION

[0010] According to the present invention, it is possible to improve the production efficiency of organic hydrides.

BRIEF DESCRIPTION OF DRAWINGS

[0011]

[Fig. 1] Fig. 1 is a schematic diagram of an organic hydride production system according to an embodiment.

[Fig. 2] Fig. 2 is a diagram showing evaluation results of the Faraday efficiency and evaluation results of water mixed into a catholyte in each of exemplary embodiments and comparative examples.

DESCRIPTION OF EMBODIMENTS

[0012] Hereinafter, the present invention will be described based on preferred embodiments with reference to the drawings. The embodiments do not limit the technical scope of the present invention and are shown for illustrative purposes, and not all the features described in the embodiments and combinations thereof are necessarily essential to the invention. Therefore, regarding the details of the embodiments, many design modifications such as change, addition, deletion, etc., of the constituent elements may be made without departing from the spirit of the invention defined in the claims. New embodiments resulting from added design change will provide the advantages of the embodiments and variations that are combined. In the embodiments, the details for which such design change is possible are emphasized with the notations "according to the embodiment," "in the embodiment," etc. However, design change is also allowed for those without such notations. Optional combinations of the constituting elements described in the embodiments are also valid as embodiments of the present invention. The same or equivalent constituting elements, members, and processes illustrated in each drawing shall be denoted by the same reference numerals, and duplicative explanations will be omitted appropriately. The scales and shapes of parts shown in each figure are set for the sake of convenience in order to facilitate the explanation and shall not be interpreted in a limited manner unless otherwise mentioned. Terms like "first," "second," etc., used in the specification and claims do not indicate an order or importance by any means and are used to distinguish a certain feature from the others. Some of the components in each figure may be omitted if they are not important for explanation.

[0013] Fig. 1 is a schematic diagram of an organic hydride production system 1 according to an embodiment. The organic hydride production system 1 as an example includes an apparatus 2 for producing an organic hydride, a catholyte supply device 4, and an anolyte supply device 6. Although only one apparatus 2 for producing an organic hydride is shown in Fig. 1, the organic hydride production system 1 may include a plurality of apparatuses 2 for producing an organic hydride. In this case, the respective apparatuses 2 for producing an organic hydride are stacked in the same direction such that the cathode electrode 10 and the anode electrode 12 are arranged in the same direction, and are electrically connected in series. Note that the apparatuses 2 for producing an organic hydride may be connected in parallel, or may be a combination of series connection and parallel connection.

[0014] The apparatus 2 for producing an organic hydride is an electrolysis cell for generating an organic hydride by hydrogenating a substance to be hydrogenated, which is a dehydrogenated product of the organic hydride, by an electrochemical reduction reaction. The apparatus 2 for producing an organic hydride includes a membrane electrode assembly 8, a pair of plate members 16a and 16b, and a pair of gaskets 18a and 18b. The membrane electrode assembly 8 includes a cathode electrode 10 (cathode), an anode electrode 12 (anode), and an electrolyte membrane 14. In the present embodiment, an explanation will be given using the membrane electrode assembly 8 as an example, and the apparatus 2 for producing an organic hydride may have a so-called zero-gap electrode structure in which an electrode having an anode catalyst applied to a hard support substrate is in physical contact with the electrolyte membrane.

[0015] The cathode electrode 10 produces an organic hydride and hydroxide ions from the substance to be hydrogenated and water. The cathode electrode 10 contains precious metals such as platinum (Pt), ruthenium (Ru), and palladium (Pd) and base metals such as nickel (Ni) as a cathode catalyst for hydrogenating the substance to be hydrogenated with water. It is preferable that the cathode electrode 10 also contains a porous catalyst support that supports the cathode catalyst. The catalyst support includes an electron-conductive material such as porous carbon, a porous metal, or a porous metal oxide.

[0016] Furthermore, the cathode catalyst is coated with an anion-exchange ionomer. For example, the catalyst support in the state of supporting the cathode catalyst is coated with an ionomer. Examples of the ionomer include polymers such as Fumion (registered trademark). It is preferable that the cathode catalyst is partially coated with the ionomer. As a result,

it is possible to efficiently supply three elements (the substance to be hydrogenated, water, and an electron) necessary for an electrochemical reaction in the cathode electrode 10 to the reaction field.

[0017] As an example, the cathode electrode 10 has a catalyst layer 10a and a diffusion layer 10b. The catalyst layer 10a is disposed closer to the electrolyte membrane 14 than the diffusion layer 10b. The catalyst layer 10a contains the cathode catalyst, the catalyst support, and the ionomer described above. The diffusion layer 10b is in contact with a main surface of the catalyst layer 10a on a side opposite to the electrolyte membrane 14. The diffusion layer 10b uniformly diffuses the substance to be hydrogenated supplied from the outside into the catalyst layer 10a. The organic hydride generated in the catalyst layer 10a is discharged to the outside of the cathode electrode 10 through the diffusion layer 10b. The diffusion layer 10b includes a conductive material such as carbon or a metal. In addition, the diffusion layer 10b is a porous body such as a sintered body of fibers or particles or a foamed molded body. Examples of the material included in the diffusion layer 10b include a carbon woven fabric (carbon cloth), a carbon nonwoven fabric, and carbon paper. Note that the diffusion layer 10b may be omitted.

[0018] The anode electrode 12 oxidizes the hydroxide ions so as to produce oxygen. The anode electrode 12 has a metal such as iridium (Ir), ruthenium (Ru), platinum (Pt), iron (Fe), cobalt (Co), nickel (Ni), and an oxide thereof, a carbon material such as graphene, and a partial oxide thereof as an anode catalyst for oxidizing hydroxide ions. The anode catalyst may be dispersedly supported or coated on a base material having electron conductivity. The base material includes a material containing, for example, a metal such as titanium (Ti) or stainless steel (SUS) as a main component. Examples of the form of the base material include a woven fabric sheet or a nonwoven fabric sheet, a mesh, a porous sintered body, a foamed molded body (foam), and an expanded metal.

[0019] The electrolyte membrane 14 is disposed between the cathode electrode 10 and the anode electrode 12. The electrolyte membrane 14 is composed of an anion exchange membrane and moves hydroxide ions from the cathode electrode 10 side to the anode electrode 12 side. Examples of the anion exchange membrane that can be used for the electrolyte membrane 14 include a known anion exchange membrane such as Fumasep (registered trademark) (manufactured by FuMA-Tech). Further, the electrolyte membrane 14 is more preferably composed of a polymer having a main chain resistant to the substance to be hydrogenated. Examples of such a polymer include a polymer having an aromatic ring in the main chain skeleton, such as a polyarylene. Since the electrolyte membrane 14 has a rigid skeleton such as polyarylene, resistance to the substance to be hydrogenated can be increased. Thereby, cross-leakage of the substance to be hydrogenated to the anode electrode side can be further suppressed.

[0020] The plate member 16a and the plate member 16b are made of a metal such as stainless steel or titanium, for example. The plate member 16a is stacked on the membrane electrode assembly 8 from the side of the cathode electrode 10. The plate member 16b is stacked on the membrane electrode assembly 8 from the side of the anode electrode 12. Accordingly, the membrane electrode assembly 8 is sandwiched between the pair of plate members 16a and 16b. A gap between the plate member 16a and the membrane electrode assembly 8 is sealed with the gasket 18a. A gap between the plate member 16b and the membrane electrode assembly 8 is sealed with the gasket 18b. When the organic hydride production system 1 includes only one organic hydride production apparatus 2, the pair of plate members 16a and 16b can correspond to so-called end plates. When the organic hydride production system 1 includes a plurality of apparatuses 2 for producing an organic hydride, and another apparatus 2 for producing an organic hydride is arranged next to the plate member 16a or the plate member 16b, the plate member can correspond to a so-called separator.

[0021] The cathode flow path 20 is connected to the cathode electrode 10. The cathode flow path 20 feeds and discharges a catholyte LC to and from the cathode electrode 10. A groove may be provided on a main surface facing the cathode electrode 10 side in the plate member 16a, and this groove may constitute the cathode flow path 20.

[0022] The anode flow path 22 is connected to the anode electrode 12. The anode flow path 22 feeds and discharges an anolyte LA to and from the anode electrode 12. A groove may be provided on a main surface facing the anode electrode 12 side in the plate member 16b, and this groove may constitute the anode flow path 22.

[0023] The catholyte LC is supplied to the cathode electrode 10 by the catholyte supply device 4. The catholyte supply device 4 has a catholyte tank 24, a first cathode pipe 26, a second cathode pipe 28, and a cathode pump 30. The catholyte LC is stored in the catholyte tank 24. The catholyte LC contains an organic hydride raw material, i.e., the substance to be hydrogenated. As an example, the catholyte LC does not contain an organic hydride before the start of the operation of the organic hydride production system 1, and after the start of the operation, the organic hydride generated by electrolysis is mixed in, whereby the catholyte becomes the liquid mixture of the substance to be hydrogenated and the organic hydride. The substance to be hydrogenated and the organic hydride are preferably a liquid at 20°C and 1 atm.

[0024] The substance to be hydrogenated and the organic hydride are not particularly limited as long as they are organic compounds capable of adding/desorbing hydrogen by reversibly causing a hydrogenation reaction/dehydrogenation reaction. As the substance to be hydrogenated and the organic hydride used in the present embodiment, an acetone-isopropanol type, a benzoquinone-hydroquinone type, an aromatic hydrocarbon type, and the like can be widely used. Among these, the aromatic hydrocarbon type is preferable from the viewpoint of transportability during energy transport or the like. In general, aromatic hydrocarbon-based substances to be hydrogenated and organic hydrides are hydrophobic and phase-separate from water at 20°C and 1 atm.

[0025] An aromatic hydrocarbon compound used as the substance to be hydrogenated is a compound containing at least one aromatic ring. Examples of the aromatic hydrocarbon compound include benzene, alkylbenzene, naphthalene, alkylnaphthalene, anthracene, diphenylethane, tetralin, and the like. The alkylbenzene contains a compound in which 1 to 4 hydrogen atoms in the aromatic ring are substituted with a linear alkyl group or a branched alkyl group having 1 to 6 carbons. Examples of such a compound include toluene, xylene, mesitylene, ethylbenzene, and diethylbenzene. The alkylnaphthalene contains a compound in which 1 to 4 hydrogen atoms in the aromatic ring are substituted with a linear alkyl group or a branched alkyl group having 1 to 6 carbons. Examples of such a compound include methylnaphthalene. These compounds may be used alone or in combination.

[0026] The substance to be hydrogenated is preferably at least one of toluene and benzene. It is also possible to use a nitrogen-containing heterocyclic aromatic compound such as quinoline, isoquinoline, N-alkylpyrrole, N-alkylindole, or N-alkyldibenzopyrrole as the substance to be hydrogenated. The organic hydride is obtained by hydrogenating the above-described substance to be hydrogenated, and examples thereof include cyclohexane, methylcyclohexane, dimethylcyclohexane, and decahydroquinoline.

[0027] The catholyte tank 24 is connected to the cathode electrode 10 by the first cathode pipe 26. One end of the first cathode pipe 26 is connected to the catholyte tank 24, and the other end of the first cathode pipe 26 is connected to the entrance of the cathode flow path 20. The cathode pump 30 is provided in the middle of the first cathode pipe 26. The cathode pump 30 can be constituted by a known pump such as a gear pump or a cylinder pump, for example. Note that the catholyte supply device 4 may circulate the catholyte LC using a liquid feeding device other than the pump. The catholyte tank 24 is connected to the cathode electrode 10 also by the second cathode pipe 28. One end of the second cathode pipe 28 is connected to the exit of the cathode flow path 20, and the other end of the second cathode pipe 28 is connected to the catholyte tank 24.

[0028] The catholyte LC in the catholyte tank 24 flows into the cathode electrode 10 through the first cathode pipe 26 by driving of the cathode pump 30. The catholyte LC flowing into the cathode electrode 10 is subjected to an electrode reaction in the cathode electrode 10. The catholyte LC in the cathode electrode 10 is returned to the catholyte tank 24 through the second cathode pipe 28. As an example, the catholyte tank 24 also functions as a gas-liquid separator. The hydrogen gas may be generated by the side reaction in the cathode electrode 10. Therefore, the hydrogen gas may be mixed in the catholyte LC discharged from the cathode electrode 10. The catholyte tank 24 separates the hydrogen gas in the catholyte LC from the catholyte LC and discharges the hydrogen gas to the outside of the system.

[0029] The electrolyte membrane 14 according to the present embodiment is composed of an anion exchange membrane. Thereby, as will be described in detail later, the movement of an excessive amount of water from the anode electrode 12 to the cathode electrode 10 is suppressed. Therefore, theoretically, the mixing of water into the catholyte LC can be suppressed to a negligible extent. However, the catholyte supply device 4 may be provided with an oil-water separator for separating water from the catholyte LC as necessary. Alternatively, the catholyte tank 24 may function as an oil-water separator.

[0030] In the catholyte supply device 4 according to the present embodiment, the catholyte LC is circulated between the cathode electrode 10 and the catholyte tank 24. However, the present invention is not limited to this configuration, and the catholyte LC may be sent to the outside of the system from the cathode electrode 10 without being returned to the catholyte tank 24.

[0031] The anolyte LA is supplied to the anode electrode 12 by the anolyte supply device 6. The anolyte supply device 6 has an anolyte tank 32, a first anode pipe 34, a second anode pipe 36, and an anode pump 38. The anolyte LA is stored in the anolyte tank 32. The anolyte LA contains water. Examples of the anolyte LA include an alkaline solution such as: an aqueous solution of potassium hydroxide; ion-exchanged water; and an aqueous solution containing an inorganic electrolyte such as potassium sulfate.

[0032] The anolyte tank 32 is connected to the anode electrode 12 by the first anode pipe 34. One end of the first anode pipe 34 is connected to the anolyte tank 32, and the other end of the first anode pipe 34 is connected to the entrance of the anode flow path 22. The anode pump 38 is provided in the middle of the first anode pipe 34. The anode pump 38 can be constituted by a known pump such as a gear pump or a cylinder pump, for example. Note that the anolyte supply device 6 may circulate the anolyte LA using a liquid feeding device other than the pump. The anolyte tank 32 is connected to the anode electrode 12 by the second anode pipe 36. One end of the second anode pipe 36 is connected to the exit of the anode flow path 22, and the other end of the second anode pipe 36 is connected to the anolyte tank 32.

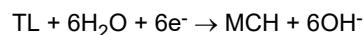
[0033] The anolyte LA in the anolyte tank 32 flows into the anode electrode 12 through the first anode pipe 34 by driving of the anode pump 38. A part of the water in the anolyte LA flowing into the anode electrode 12 diffuses to the cathode electrode 10 side via the electrolyte membrane 14 and is subjected to the electrode reaction at the cathode electrode 10. The anolyte LA in the anode electrode 12 is returned to the anolyte tank 32 through the second anode pipe 36. As an example, the anolyte tank 32 also functions as a gas-liquid separator. In the anode electrode 12, oxygen gas is generated by the electrode reaction. Therefore, the oxygen gas is mixed into the anolyte LA discharged from the anode electrode 12. The anolyte tank 32 separates the oxygen gas in the anolyte LA from the anolyte LA and discharges the oxygen gas to the outside of the system.

[0034] In the anolyte supply device 6 according to the present embodiment, the anolyte LA is circulated between the anode electrode 12 and the anolyte tank 32. However, the present invention is not limited to this configuration, and the anolyte LA may be sent from the anode electrode 12 to the outside of the system without being returned to the anolyte tank 32.

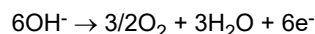
[0035] The apparatus 2 for producing an organic hydride is supplied with power from an external power supply (not shown). When power is supplied from the power supply to the apparatus 2 for producing an organic hydride, a predetermined cell voltage is applied between the cathode electrode 10 and the anode electrode 12 of the apparatus 2 for producing an organic hydride, and an electrolytic current flows. The power supply sends power supplied from a power supply device to the apparatus 2 for producing an organic hydride. The power supply device can be constituted by a power generation device that generates power using renewable energy, for example, a wind power generation device, a solar power generation device, or the like. Note that the power supply device is not limited to such a renewable energy power generation device, and may be a system power supply, a storage device storing power from the power generation device using renewable energy or the system power supply, or the like. A combination of two or more of these devices may be used. Further, the configuration of the organic hydride production system 1 is not limited to those described above, and the configuration of each part can be appropriately changed.

[0036] A reaction that occurs in a case where toluene (TL) is used as an example of the substance to be hydrogenated in the organic hydride production apparatus 2 is as follows. The organic hydride obtained in a case where toluene is used as the substance to be hydrogenated is methylcyclohexane (MCH).

<Electrode Reaction in Cathode Electrode>



<Electrode Reaction in Anode Electrode>



[0037] That is, the electrode reaction in the cathode electrode 10 and the electrode reaction in the anode electrode 12 proceed in parallel. At the cathode electrode 10, toluene is hydrogenated with water so as to produce methylcyclohexane and hydroxide ions. The hydroxide ions generated at the cathode electrode 10 pass through the electrolyte membrane 14 and move to the anode electrode 12. The hydroxide ions supplied to the anode electrode 12 are oxidized at the anode electrode 12 so as to generate oxygen, water, and electrons. The electrons generated by the oxidation of the hydroxide ions are supplied to the cathode electrode 10 via an external circuit and are used for electrode reaction at the cathode electrode 10.

[0038] Therefore, according to the apparatus 2 for producing an organic hydride according to the present embodiment, the oxidation reaction of the hydroxide ions and the hydrogenation reaction of the substance to be hydrogenated can be performed in one step. For this reason, organic hydride production efficiency can be increased as compared with a conventional technique in which the organic hydride is produced by a two-step process which includes a process of producing hydrogen by water electrolysis or the like and a process of chemically hydrogenating the substance to be hydrogenated in a reactor such as a plant. Furthermore, since the reactor for performing the chemical hydrogenation and a high-pressure vessel for storing the hydrogen produced by the water electrolysis or the like are not required, a significant reduction in facility cost can be achieved.

[0039] Further, the apparatus 2 for producing an organic hydride according to the present embodiment is an anion exchange membrane (AEM) type, and moves hydroxide ions from the cathode electrode 10 to the anode electrode 12. Therefore, the direction of ion movement is opposite to that of the conventional proton exchange membrane (PEM) type apparatus. In this case, the movement of water from the anode electrode 12 side to the cathode electrode 10 side is theoretically only diffusion by the concentration gradient of water. Hereinafter, water that moves from one electrode side to the other electrode side due to the water concentration gradient is referred to as "physical diffusion water" as appropriate. In the case of the AEM type, the water concentration of the anode is higher than that of the cathode. Therefore, the physical diffusion water moves from the anode electrode 12 side to the cathode electrode 10 side. In the AEM type, the flow of electroosmotic water is in the direction from the cathode electrode 10 side to the anode electrode 12 side. Therefore, the water moving from the anode electrode 12 side to the cathode electrode 10 side does not contain electroosmotic water and contains only physical diffusion water. For this reason, the entry of an excessive amount of water into the cathode electrode 10 can be suppressed, and the inhibition of the diffusion of the substance to be hydrogenated due to the water in the cathode electrode 10 can be suppressed. Note that although the water originally held by the electrolyte membrane 14 can also enter the cathode electrode 10 as part of the physical diffusion water, the amount of this water is also a small amount compared to the amount of electroosmotic water in the PEM type device.

[0040] This allows the substance to be hydrogenated to reach the reaction field easily. Therefore, the shortage of the substance to be hydrogenated can be avoided, and the occurrence of side reactions can be suppressed. Therefore, the efficiency of the electrode reaction at the cathode electrode 10, that is, a decrease in Faraday efficiency, can be suppressed. In particular, it is possible to suppress a decrease in reaction efficiency when a catholyte with a low concentration of the substance to be hydrogenated is supplied to the cathode electrode 10. As a result, the production

efficiency of the organic hydride is improved. Further, since the accumulation of water in the cathode electrode 10 can be suppressed, the process of separating the organic hydride and water from each other becomes easier or can be omitted. In this respect, the production efficiency of organic hydride is also improved.

[0041] In the case of the PEM type, water locally disappears near the interface between the anode catalyst layer and the electrolyte membrane due to the electrode reaction at the anode electrode. On the other hand, a large amount of electroosmotic water exists near the interface between the cathode catalyst layer and the electrolyte membrane. Therefore, the water on the cathode electrode side can return to the anode electrode side due to the concentration gradient of water. For this reason, the direction of movement of the physical diffusion water is opposite to that of the AEM type. Further, when the anolyte LA is, for example, a solution containing a supporting electrolyte, water can return from the cathode electrode side to the anode electrode side due to the osmotic pressure caused by the concentration gradient of the electrolyte. Hereinafter, water that moves from one electrode side to the other electrode side due to the electrolyte concentration gradient is referred to as "osmotic pressure transfer water" as appropriate. In the case of the PEM type, the osmotic pressure transfer water moves from the cathode electrode 10 side to the anode electrode 12 side.

[0042] Therefore, in the PEM type, the physical diffusion water and the osmotic pressure transfer water move from the cathode electrode side to the anode electrode side. Hereinafter, the water moving from the cathode electrode side to the anode electrode side (physical diffusion water + osmotic pressure transfer water) in the PEM type is referred to as "back-diffusion water" as appropriate. "Back" in "back-diffusion water" means that the direction is opposite to the direction of ion movement. Further, the phenomenon where the back-diffusion water returns to the anode electrode side that occurs in the PEM type is called "back diffusion of water."

[0043] When back diffusion of water occurs, a small amount of the substance to be hydrogenated dissolved in the water can also move to the anode electrode side along with the water. As a result of this, the anode catalyst can be deactivated by the substance to be hydrogenated. On the other hand, since the accumulation of water in the cathode electrode 10 is suppressed in the present embodiment, the movement of water from the cathode electrode 10 side to the anode electrode 12 side is also suppressed. Therefore, it is possible to suppress the deactivation of the anode catalyst by the substance to be hydrogenated. Further, the loss of the substance to be hydrogenated from the cathode electrode 10 can also be suppressed. As a result, the production efficiency of the organic hydride is improved.

[0044] In the case of the PEM type, the reaction proceeds by the movement of protons from the anolyte to the cathode electrode side in the state of oxonium ions. Therefore, it is necessary to secure a proton (oxonium ion) conduction path in the anolyte. Therefore, from the viewpoint of reaction promotion, proton activity, and the like, the anolyte is preferably neutral to acidic. Further, from the viewpoint of efficient proton conduction, the anode catalyst and the cathode catalyst are preferably coated with strongly acidic proton exchange ionomers. Therefore, the anode catalyst and the cathode catalyst are placed in an acidic atmosphere. For this reason, each catalyst is limited to what can be used in an acidic atmosphere. In particular, the anode catalyst is limited to materials that are resistant to acidic and oxidizing atmospheres.

[0045] On the other hand, hydroxide ions move from the cathode electrode 10 side to the anode electrode 12 side in the present embodiment. For this reason, the anolyte is preferably neutral to alkaline. Further, from the viewpoint of efficient hydroxide ion conduction, the anode catalyst and cathode catalyst are preferably coated with alkaline anion-exchange ionomers. Therefore, the anode catalyst and the cathode catalyst are placed in a neutral to alkaline atmosphere. For this reason, each catalyst may be usable in a neutral to alkaline atmosphere. There are more options for the anode catalyst that can be used in a neutral to alkaline atmosphere than in an acidic atmosphere. Therefore, according to the present embodiment, the degree of design freedom of the apparatus 2 for producing an organic hydride can be increased, making it easy to reduce the cost of the members and the like.

[0046] The lower the solubility of the substance to be hydrogenated and the organic hydride in water is, the more effective it is to suppress the movement of water from the anode electrode 12 side to the cathode electrode 10 side. For example, the suppression of water movement is more effective when the solubility in water at 25°C of at least one of the substance to be hydrogenated and the organic hydride is preferably 3 g/100 mL or less and more preferably 2 g/100 mL or less. The removal of water by the substance to be hydrogenated and the organic hydride becomes significantly difficult when the solubility in water of at least one of the substance to be hydrogenated and the organic hydride is 3 g/100 mL or less. Therefore, the suppression of water movement is more effective. Examples of the substance to be hydrogenated and the organic hydride that are particularly expected to have this effect include benzene (0.18 g/100 mL H₂O) and cyclohexane (0.36 g/100 mL H₂O), toluene (0.05 g/100 mL H₂O) and methylcyclohexane (1.6 g/100 mL H₂O), naphthalene (0.003 g/100 mL H₂O) and decahydronaphthalene (0.001 g/100 mL H₂O), and the like.

[0047] The water used for the electrode reaction at the cathode electrode 10 is preferably provided from physical diffusion water entering from the electrolyte membrane 14. The physical diffusion water includes at least one of the water derived from the anolyte LA and the water originally held by the electrolyte membrane 14. That is, the water in the anolyte LA diffuses from the anode electrode 12 side to the cathode electrode 10 side via the electrolyte membrane 14 due to the concentration gradient of water. Further, the electrolyte membrane 14 may absorb and retain water in the atmosphere. Alternatively, the electrolyte membrane 14 can be subjected to a water impregnation treatment when assembling the apparatus 2 for producing an organic hydride. This water can also enter the cathode electrode 10 side due to the

concentration gradient of water.

[0048] The amount of water entering from the electrolyte membrane 14 to the cathode electrode 10 side is preferably adjusted to an amount necessary and sufficient for hydrogenating the substance to be hydrogenated at the cathode electrode 10 and not inhibiting the substance to be hydrogenated from reaching the reaction field. If the amount of water entering the cathode electrode 10 side is insufficient, not only will there be a shortage of water as a substrate, but the ionomers in the cathode catalyst layer will not be wetted, making it difficult to form ion conduction paths between the ion exchange groups. Therefore, the hydrogenation of the substance to be hydrogenated can be inhibited. Conversely, if the amount of water entering the cathode electrode 10 side becomes excessive, the arrival of the substance to be hydrogenated to the reaction field can be inhibited. As a result, hydrogen generation due to a side reaction can become dominant at the cathode electrode 10. The amount of water is determined by the physical diffusion water and the osmotic transfer water that are via the electrolyte membrane 14. Therefore, the amount of water can be controlled by the material and film thickness of the electrolyte membrane 14, the operating temperature of the apparatus 2 for producing an organic hydride, the support electrolyte concentration of the anolyte, and the like. The amount of water can be defined, for example, by a unit time during non-electrolysis and the amount of water per area of the electrolyte membrane 14 (mg/min/m²). Further, the appropriate range of the amount of water is preferably 1.05 to 1.70/min, for example, when expressed as the ratio (/min) of the physical amount of water per unit time during non-electrolysis and area of the electrolyte membrane 14 to the number of ion exchange groups (mmol/m²) per area of the ionomers in the cathode catalyst layer. By setting the amount of water to 1.05/min or more, it is possible to more reliably suppress a decrease in the performance of the apparatus 2 for producing an organic hydride due to inhibition of hydrogenation caused by a lack of water. Further, by setting the amount of water to 1.70/min or less, it is possible to more reliably suppress the inhibition of the reaction due to the accumulation of excess water in the cathode catalyst layer.

[0049] The cathode electrode 10 uses at least one of water derived from the anolyte LA and water derived from the electrolyte membrane 14 that has entered the cathode electrode 10 from the electrolyte membrane 14 for a reaction with the substance to be hydrogenated. Thereby, compared to the case where water is directly supplied to the cathode electrode 10 from the outside of the apparatus 2 for producing an organic hydride, it is easier to suppress the inhibition of the diffusion of the substance to be hydrogenated due to water, the complication of the recovery process of the organic hydride, the occurrence of back diffusion of water, and the like. Although the water used in the cathode electrode 10 is preferably only water entering from the electrolyte membrane 14, direct water absorption from the outside into the cathode electrode 10 may be appropriately combined.

[0050] The embodiments may be defined by the items described in the following.

[Item 1]

[0051] An apparatus (2) for producing an organic hydride including:

- a cathode electrode (10) that generates an organic hydride and hydroxide ions from a subject to be hydrogenated and water;
- an anode electrode (12) that produces oxygen by oxidizing the hydroxide ions; and
- an electrolyte membrane (14) that is composed of an anion exchange membrane and is arranged between the cathode electrode (10) and the anode electrode (12) so as to transfer the hydroxide ions from the cathode electrode (10) side to the anode electrode (12) side.

[Item 2]

[0052] The apparatus (2) for producing an organic hydride according to Item 1, wherein

- the anode electrode (12) is supplied with an anolyte (LA) containing water,
- the electrolyte membrane (14) contains water, and
- the cathode electrode (10) uses water entering from the electrolyte membrane (14) for a reaction with the substance to be hydrogenated.

[Item 3]

[0053] A method for producing an organic hydride in which the apparatus (2) for producing an organic hydride according to Item 1 or 2 is used, including:

- producing an organic hydride and hydroxide ions from the substance to be hydrogenated and water at the cathode electrode (10) ;

moving the hydroxide ions to the anode electrode (12) via the electrolyte membrane (14); and producing oxygen by oxidizing the hydroxide ions at the anode electrode (12).

Exemplary Embodiments

[0054] Hereinafter, exemplary embodiments of the present invention will be explained. However, these exemplary embodiments are merely examples for suitably explaining the present invention and do not limit the present invention in any way.

(First Exemplary Embodiment)

[0055] A quaternary ammonium-based AEM-type electrolyte membrane (Fumasep (registered trademark) FAA-3-PK-130, manufactured by FuMA-Tech) having a polyarylene skeleton was prepared. The thickness of this electrolyte membrane was 130 μm . The degree of water permeability during non-electrolysis in the electrolyte membrane was measured according to the following procedure.

[0056] That is, the electrolyte membrane was cut out into a circle having ϕ of 40 mm. An electrolyte membrane sandwiched between circular Viton (registered trademark) gaskets was fixed between two flange glass cells of an H-type cell (VB9B, manufactured by EC FRONTIER CO., LTD). The exposed portion of the electrolyte membrane had ϕ of 28 mm. The flange glass cell on one side was filled with 25 mL of 1 mol/L KOH aqueous solution. The weight of the entire H-type cell was measured, and the measured weight was set as a starting weight (A_{mg}). The openings of the flange glass cells on the respective sides were sealed with parafilms and left to stand. After a predetermined time, the parafilms sealing the openings were removed, and the water diffused into the flange glass cell on the side not filled with the KOH solution was wiped off. The weight of the entire H-type cell was measured again, and the measured weight was set as an ending weight (B_{mg}). Then, based on the following equation (1), the permeability of water during non-electrolysis was calculated.

$$(A-B) [\text{mg}]/\text{standing time} [\text{min}]/\text{area of exposed part of electrolyte membrane} [\text{m}^2] \quad \text{Equation (1):}$$

[0057] An anode catalyst ink was prepared by mixing an IrO_2 catalyst (manufactured by Furuya Metal Co., Ltd.), a quaternary ammonium-based anion-exchange ionomer (Fumion (registered trademark) FAA-3-SOLUT-10, manufactured by FuMA-Tech), pure water, and 1-propanol (manufactured by FUJIFILM Wako Pure Chemical Corporation). The catalyst support density of the anode catalyst ink was 1.5 mg/cm^2 , and the ionomer/catalyst ratio (I/Cat) was 0.1. An anode catalyst layer was formed by applying a prepared anode catalyst ink to one of the main surfaces of the above-described AEM-type electrolyte membrane.

[0058] A cathode catalyst ink was prepared by mixing PtRu / C catalyst (TEC61E54, manufactured by TANAKA PRECIOUS METAL TECHNOLOGIES Co., Ltd.), a quaternary ammonium-based anion-exchange ionomer (Fumion (registered trademark) FAA-3-SOLUT-10, manufactured by FuMA-Tech), pure water, and 1-propanol (manufactured by FUJIFILM Wako Pure Chemical Corporation). The catalyst support density of the cathode catalyst ink was 1 mg/cm^2 , and the ionomer/carbon ratio (I/C) was 0.8. A cathode catalyst layer was formed by applying a prepared cathode catalyst ink to the opposite main surface of the AEM-type electrolyte membrane in which an anode catalyst layer was formed on one main surface. Based on the composition of the cathode catalyst ink, the permeated water amount ratio to the ion exchange group amount of the ionomers was calculated using the following equation (2). The ion exchange capacity (IEC) of the quaternary ammonium-based anion-exchange ionomer used in the present exemplary embodiment was 1.86 mmol/g .

$$(\text{water permeability during non-electrolysis} [\text{mg}/\text{min}/\text{m}^2]/\text{molecular weight of water} [\text{g}/\text{mol}]) / (\text{ionomer content in catalyst layer} [\text{mg}/\text{m}^2] \times \text{ionomer ion exchange capacity} [\text{mmol}/\text{g}]) \quad \text{Equation (2):}$$

[0059] The apparatus for producing an organic hydride according to the first exemplary embodiment was obtained by stacking a cathode end plate, a cathode side gasket, a diffusion layer, an AEM-type electrolyte membrane having a cathode catalyst layer and an anode catalyst layer stacked thereon, an anode side gasket, and an anode end plate in the order stated. For each end plate, a titanium plate with a flow path for each solution was used. Each gasket was manufactured by Viton (registered trademark). The electrode effective area of the apparatus for producing an organic hydride was 25 cm^2 .

[0060] Toluene serving as a catholyte was circulated to the cathode of the apparatus for producing an organic hydride at a flow rate of 20 mL/min. Further, a 1 mol/L KOH aqueous solution serving as an anolyte was circulated at the anode at a flow rate of 20 mL/min. Then, an electrolytic reaction was performed at a temperature of 60°C and a predetermined cell voltage. The Faraday efficiency was calculated from the amount of electricity consumed by the electrolytic reaction and the amount of organic hydride generated. Then, the Faraday efficiency of 80% or more is evaluated as $\circ$, and the Faraday

efficiency of less than 80% is evaluated as $\times$. Further, after the electrolytic reaction, the amount of water in the catholyte was measured by separating and weighing the aqueous layer in a catholyte container. Then, a ratio of water mixed in the entire catholyte after electrolysis of less than 1% was evaluated as $\circ$, and a ratio of water mixed in the entire catholyte after electrolysis of 1% or more was evaluated as x . The results are shown in Fig. 2.

(Second Exemplary Embodiment)

[0061] The water permeability measurement, the preparation of an apparatus for producing an organic hydride, the electrolysis treatment, the calculation of the permeated water amount ratio, and each evaluation were carried out in the same manner as in the first exemplary embodiment, except that ion-exchanged water was used for the water permeability measurement and the anolyte. The results are shown in Fig. 2.

(First Comparative Example)

[0062] A polyfluorosulfonic acid-based PEM-type electrolyte membrane (Nafion (registered trademark) 117, manufactured by The Chemours Company) was prepared. The thickness of this electrolyte membrane was 180 μm . The degree of water permeability in this electrolyte membrane was measured in the same manner as in the second exemplary embodiment.

[0063] An anode catalyst ink was prepared by mixing an IrO_2 catalyst (manufactured by Furuya Metal Co., Ltd.), a polyfluorosulfonic acid cation-exchange ionomer (Nafion (registered trademark) DE2020CS, manufactured by The Chemours Company), ion-exchanged water, and 1-propanol (manufactured by FUJIFILM Wako Pure Chemical Corporation). The catalyst support density of the anode catalyst ink was 1.5 mg/cm^2 , and the ionomer/catalyst ratio (I/Cat) was 0.1. An anode catalyst layer was formed by applying a prepared anode catalyst ink to one of the main surfaces of the above-described PEM-type electrolyte membrane.

[0064] A cathode catalyst ink was prepared by mixing a PtRu/C catalyst (TEC61E54, manufactured by TANAKA PRECIOUS METAL TECHNOLOGIES Co., Ltd.), a polyfluorosulfonic acid-based cation-exchanged ionomer (Nafion (registered trademark) DE2020CS, manufactured by The Chemours Company), ion-exchanged water, and 1-propanol (manufactured by FUJIFILM Wako Pure Chemical Corporation). The catalyst support density of the cathode catalyst ink was 1 mg/cm^2 , and the ionomer/carbon ratio (I/C) was 0.5. A cathode catalyst layer was formed by applying a prepared cathode catalyst ink to the opposite main surface of the PEM-type electrolyte membrane in which an anode catalyst layer was formed on one main surface. Based on the composition of the cathode catalyst ink, the permeated water amount ratio to the ion exchange group amount of the ionomers was calculated in the same way as in the first and second exemplary embodiments. The ion exchange capacity of the polyfluorosulfonic acid cation-exchange ionomer used in the present comparative example was 1.00 mmol/g .

[0065] The apparatus for producing an organic hydride according to the first comparative example was obtained by stacking a cathode end plate, a cathode side gasket, a diffusion layer, a PEM-type electrolyte membrane having a cathode catalyst layer and an anode catalyst layer stacked thereon, an anode side gasket, and an anode end plate in the order stated. Each end plate and each spacer were the same as those used in the first exemplary embodiment. The electrode effective area of the apparatus for producing an organic hydride was 25 cm^2 . Using the obtained apparatus for producing an organic hydride, electrolytic treatment and each evaluation were performed in the same manner as in the second exemplary embodiment. The results are shown in Fig. 2.

[0066] Fig. 2 is a diagram showing evaluation results of the Faraday efficiency and evaluation results of water mixed into a catholyte in each of exemplary embodiments and comparative examples. From the comparison between the first and second exemplary embodiments and the first comparative example, it has been confirmed that when the apparatus for producing an organic hydride includes an AEM type electrolyte membrane, the ratio of water mixed in the catholyte after electrolysis is less than 1%, which is an extremely small amount, and a Faraday efficiency of 80% or more can be obtained at least at any of the cell voltages. Therefore, it has been confirmed that the use of an AEM-type electrolyte membrane can improve the production efficiency of an organic hydride.

[0067] Further, from the comparison between the first and second exemplary embodiments, it has been confirmed that a Faraday efficiency of 80% or more can be obtained at a wider range of cell voltages when the anolyte does not contain a support electrolyte than when the anolyte contains a support electrolyte. Further, it has been confirmed that the degree of water permeability during non-electrolysis and a permeated water amount ratio to the ionomer ion exchange group amount are higher in the second exemplary embodiment than those in the first exemplary embodiment. From this, by reducing the support electrolyte concentration of the anolyte, it has been shown that the physical diffusion water moved from the anode electrode 12 side to the cathode electrode 10 side can be suppressed from returning to the anode electrode 12 side as osmotic pressure transfer water due to the concentration gradient of the support electrolyte. Thereby, more water can be supplied to the cathode electrode 10 side. Therefore, it is possible to prevent the supply of water to the cathode electrode 10 from becoming the rate-limiting factor for the cathode reaction. Therefore, the cell voltage can be increased to increase

the current density of the electrolytic reaction, in other words, the reaction rate. In all of the first and second exemplary embodiments and the first comparative example, cross leakage of toluene to the anode electrode side was not observed.

INDUSTRIAL APPLICABILITY

[0068] The present invention can be used for an apparatus for producing an organic hydride and a method for producing an organic hydride.

REFERENCE SIGNS LIST

[0069] 2 apparatus for producing an organic hydride, 10 cathode electrode, 12 anode electrode, 14 electrolyte membrane, LA anolyte, LC catholyte

Claims

1. An apparatus for producing an organic hydride comprising:

a cathode electrode that generates an organic hydride and hydroxide ions from a subject to be hydrogenated and water;
 an anode electrode that produces oxygen by oxidizing the hydroxide ions; and
 an electrolyte membrane that is composed of an anion exchange membrane and is arranged between the cathode electrode and the anode electrode so as to transfer the hydroxide ions from the cathode electrode side to the anode electrode side.

2. The apparatus for producing an organic hydride according to Claim 1, wherein

the anode electrode is supplied with an anolyte containing water,
 the electrolyte membrane contains water, and
 the cathode electrode uses water entering from the electrolyte membrane for a reaction with the substance to be hydrogenated.

3. A method for producing an organic hydride in which the apparatus for producing an organic hydride according to Claim 1 or 2 is used, comprising:

producing an organic hydride and hydroxide ions from the substance to be hydrogenated and water at the cathode electrode;
 moving the hydroxide ions to the anode electrode via the electrolyte membrane; and
 producing oxygen by oxidizing the hydroxide ions at the anode electrode.

FIG. 1

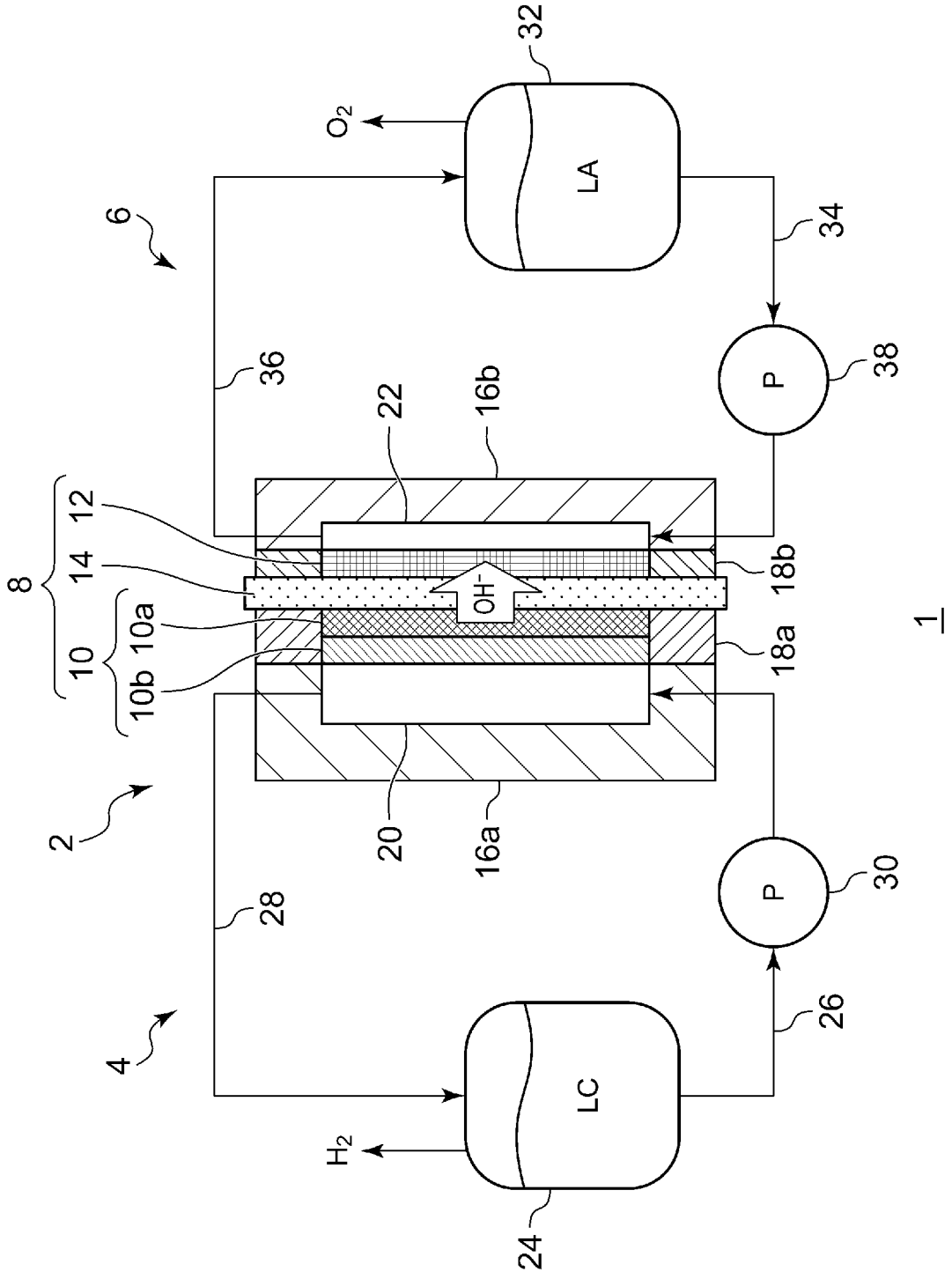


FIG. 2

		FIRST EXEMPLARY EMBODIMENT	SECOND EXEMPLARY EMBODIMENT	FIRST COMPARATIVE EXAMPLE
ELECTROLYTE MEMBRANE	TYPE	AEM	AEM	PEM
	PERMEABILITY OF WATER DURING NON-ELECTROLYSIS [mg/min/m ²]	283	453	191
PERMEATED WATER AMOUNT RATIO TO IONOMER ION EXCHANGE GROUP AMOUNT [L/min]		1.06	1.69	2.13
ANOLYTE	TYPE	1M KOH	ION-EXCHANGED WATER	ION-EXCHANGED WATER
MIXING OF WATER INTO CATHOLYTE AFTER ELECTROLYSIS		○	○	×
FARADAY EFFICIENCY	CELL VOLTAGE 1.55V	○	○	×
	CELL VOLTAGE 1.6V	○	○	×
	CELL VOLTAGE 1.9V	×	○	×

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/029965

A. CLASSIFICATION OF SUBJECT MATTER

C25B 3/25(2021.01)i; *B01J 31/08*(2006.01)i; *C25B 1/04*(2021.01)i; *C25B 3/03*(2021.01)i; *C25B 9/00*(2021.01)i;
C25B 9/23(2021.01)i; *C25B 13/04*(2021.01)i; *C25B 15/08*(2006.01)i

FI: C25B3/25; B01J31/08 Z; C25B1/04; C25B3/03; C25B9/00 A; C25B9/00 G; C25B9/23; C25B13/04 301; C25B15/08 302

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)

B01J31/08; C25B1/04; C25B3/03; C25B3/25; C25B9/00; C25B9/23; C25B13/04; C25B15/08

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, JST7580

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2020/0056292 A1 (BATTELLE ENERGY ALLIANCE, LLC) 20 February 2020 (2020-02-20) paragraphs [0021]-[0042], fig. 1-4	1-3
X	KAGESHIMA, Yosuke et al. Surface Protective and Catalytic Layer Consisting of RuO ₂ and Pt for Stable Production of Methylcyclohexane Using Solar Energy. ACS Appl. Mater. Interfaces. 2018, vol. 10, no. 51, pp. 44396-44402, https://doi.org/10.1021/acsami.8b14814 experimental section, fig. 1	1-3

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

* Special categories of cited documents:	"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
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"E" earlier application or patent but published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search

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Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/JP2023/029965

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
US	2020/0056292	A1	20 February 2020	(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

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