



(11)

EP 4 495 294 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:
22.01.2025 Bulletin 2025/04

(21) Application number: **23770159.4**

(22) Date of filing: **07.02.2023**

(51) International Patent Classification (IPC):
C25B 9/00 (2021.01) **C25B 3/03** (2021.01)
C25B 3/25 (2021.01) **C25B 9/23** (2021.01)
C25B 9/60 (2021.01) **C25B 15/02** (2021.01)

(52) Cooperative Patent Classification (CPC):
C25B 3/03; C25B 3/25; C25B 9/00; C25B 9/23;
C25B 9/60; C25B 15/02

(86) International application number:
PCT/JP2023/004020

(87) International publication number:
WO 2023/176198 (21.09.2023 Gazette 2023/38)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL
NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

(30) Priority: **17.03.2022 JP 2022042761**

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(54) **ORGANIC HYDRIDE PRODUCTION DEVICE**

(57) An organic hydride production apparatus (2) includes: a membrane electrode assembly (8) in which an anode electrode (10) and a cathode electrode (12) are laminated with a membrane (14) interposed therebetween; a supply flow path (38a) which extends in a vertical direction, and in which a catholyte (LC) flows from a lower side to an upper side; and a collection flow path (38b) which extends in the vertical direction, and in which the

catholyte (LC) flows from a lower side to an upper side. A flow resistance R1 of the catholyte (LC) flowing through the cathode electrode (12), a flow resistance R2 of the catholyte (LC) flowing through the collection flow path (38b), and a flow resistance R3 of the catholyte (LC) flowing through the supply flow path (38a) satisfy a relation of $R1 > R2 > R3$.

FIG. 5A

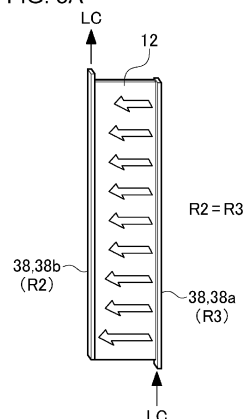
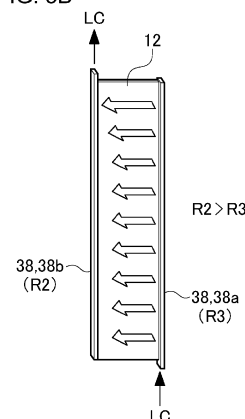


FIG. 5B



Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to an organic hydride production apparatus.

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 a technique for producing an organic hydride, a conventional organic hydride production apparatus including an anode for generating protons from water, a cathode for hydrogenating an organic compound (substance to be hydrogenated) having an unsaturated bond, and a membrane for separating the anode and the cathode is known (see, for example, Patent Literature 1). In the organic hydride production apparatus, water is supplied to the anode, a substance to be hydrogenated is supplied to the cathode, and a current is flown between the anode and the cathode, so that hydrogen is added to the substance to be hydrogenated to obtain an organic hydride.

RELATED-ART LITERATURE

PATENT LITERATURE

25 **[0004]** Patent Literature 1: WO2012/091128A

SUMMARY OF INVENTION

TECHNICAL PROBLEM

30 **[0005]** As a result of intensive studies on the above-described technique for producing an organic hydride, the present inventors have recognized that there is room for improving electrolytic performance of the organic hydride production apparatus in the conventional technique.

35 **[0006]** The present invention has been made in view of such a situation, and an object thereof is to provide a technique for improving electrolytic performance of an organic hydride production apparatus.

SOLUTION TO PROBLEM

40 **[0007]** One aspect of the present invention is an organic hydride production apparatus. This organic hydride production apparatus includes: a membrane electrode assembly in which an anode electrode that oxidizes water in an anolyte to generate protons and a cathode electrode that hydrogenates a substance to be hydrogenated in a catholyte with the protons to generate an organic hydride are laminated with a membrane that moves the protons from an anode electrode side to a cathode electrode side interposed therebetween; a supply flow path which extends in a vertical direction, in which the catholyte flows from a lower side to an upper side, and through which the catholyte is sent to the cathode electrode; and
45 a collection flow path which extends in the vertical direction and into which the catholyte flows from the cathode electrode. A flow resistance R1 of the catholyte flowing through the cathode electrode, a flow resistance R2 of the catholyte flowing through the collection flow path, and a flow resistance R3 of the catholyte flowing through the supply flow path satisfy a relation of $R1 > R2 > R3$.

50 **[0008]** Any combinations of the above components and conversion of the expressions in the present disclosure between methods, devices, systems, and the like are also effective as aspects of the present disclosure.

ADVANTAGEOUS EFFECTS OF INVENTION

55 **[0009]** According to the present invention, electrolytic performance of an organic hydride production apparatus can be improved.

BRIEF DESCRIPTION OF DRAWINGS

[0010]

- 5 [Fig. 1] Fig. 1 is a schematic diagram of an organic hydride production system according to an embodiment.
 [Fig. 2] Fig. 2 is a cross-sectional view of an organic hydride production apparatus.
 [Fig. 3] Fig. 3 is a cross-sectional view taken along the line A-A of Fig. 2.
 [Fig. 4] Fig. 4 is a schematic diagram of a membrane electrode assembly and a cathode flow path viewed from a lamination direction of an electrode and a membrane.
 10 [Fig. 5] Fig. 5A is a schematic diagram showing a flow of a catholyte when a flow resistance in a collection flow path is equal to a flow resistance in a supply flow path.
 Fig. 5B is a schematic diagram showing a flow of the catholyte when the flow resistance in the collection flow path is larger than the flow resistance in the supply flow path.
 [Fig. 6] Fig. 6 is a diagram showing a differential pressure in a cathode electrode and a toluene concentration at
 15 Faraday efficiency of 95% in each organic hydride production apparatus of each Example and each Comparative Example.

DESCRIPTION OF EMBODIMENTS

- 20 **[0011]** Hereinafter, the present invention will be described based on preferred embodiments with reference to the drawings. The embodiments are illustrative rather than limiting the technical scope of the present invention, and all features described in the embodiments and combinations thereof are not necessarily essential to the invention. Therefore, the contents of the embodiments can be subjected to many design changes such as changes, additions, and deletions of components without departing from the spirit of the invention defined in the claims. A new embodiment to which the design
 25 change is made has the effect of the combined embodiments and modifications. In the embodiment, the contents that can be subjected to such design changes are emphasized with notations such as "of the present embodiment" and "in the present embodiment", but the design changes are allowed even in the contents without such notations. Any combination of the components described in the embodiment is also effective as an aspect of the present invention. The same or equivalent components, members, and processes illustrated in the drawings are denoted by the same reference
 30 numerals, and redundant description will be omitted as appropriate. In addition, the scale and shape of each part illustrated in each drawing are set for convenience in order to facilitate the description, and are not to be limitedly interpreted unless otherwise specified. Furthermore, when the terms "first", "second", and the like are used in the present specification or claims, the terms do not represent any order or importance, but are used to distinguish one configuration from another configuration. In addition, in each drawing, some of members that are not important for describing the
 35 embodiments are omitted.

[0012] Fig. 1 is a schematic diagram of an organic hydride production system 1 according to the embodiment. The organic hydride production system 1 as an example includes an organic hydride production apparatus 2, an anolyte supply device 4, and a catholyte supply device 6.

- [0013]** The organic hydride production apparatus 2 is an electrolyzer for generating an organic hydride by hydrogenating
 40 a substance to be hydrogenated which is a dehydrogenated product of the organic hydride by an electrochemical reduction reaction. The organic hydride production apparatus 2 includes a membrane electrode assembly 8. The membrane electrode assembly 8 has a structure in which an anode electrode 10 and a cathode electrode 12 are laminated with a membrane 14 interposed therebetween. Although only one organic hydride production apparatus 2 is shown in Fig. 1, the organic hydride production system 1 may include a plurality of organic hydride production apparatuses
 45 2. In this case, the respective organic hydride production apparatuses 2 are laminated in the same direction such that the anode electrode 10 and the cathode electrode 12 are arranged in the same direction. As a result, the organic hydride production apparatuses 2 are electrically connected in series. Note that the organic hydride production apparatuses 2 may be connected in parallel, or may be a combination of series connection and parallel connection.

- [0014]** The anode electrode 10 (anode) oxidizes water in an anolyte LA to generate protons. The anode electrode 10
 50 has, for example, a metal such as iridium (Ir), ruthenium (Ru), or platinum (Pt), or a metal oxide thereof as an anode catalyst. 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.

- [0015]** The cathode electrode 12 (cathode) hydrogenates a substance to be hydrogenated in a catholyte LC with protons
 55 to generate an organic hydride. The cathode electrode 12 contains, for example, platinum or ruthenium as a cathode catalyst for hydrogenating the substance to be hydrogenated. It is preferable that the cathode electrode 12 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. Furthermore, the cathode catalyst is coated with an ionomer (cation exchange ionomer). For example, the catalyst support which is in the state of supporting the cathode catalyst is coated with an ionomer. Examples of the ionomer include a perfluorosulfonic acid polymer such as Nafion (registered trademark) or Flemion (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, a proton, and an electron) necessary for an electrochemical reaction in the cathode electrode 12 to the reaction field.

[0016] The membrane 14 is sandwiched between the anode electrode 10 and the cathode electrode 12. The membrane 14 of the present embodiment includes a solid polymer electrolyte membrane having proton conductivity, and transfers protons from the side of the anode electrode 10 to the side of the cathode electrode 12. The solid polymer electrolyte membrane is not particularly limited as long as it is a material through which protons conduct, and examples thereof include a fluorine-based ion exchange membrane having a sulfonate group.

[0017] The anolyte LA is supplied to the anode electrode 10 by the anolyte supply device 4. The anolyte LA contains water to be supplied to the anode electrode 10. Examples of the anolyte LA include an aqueous sulfuric acid solution, an aqueous nitric acid solution, an aqueous hydrochloric acid solution, pure water, and ion-exchanged water.

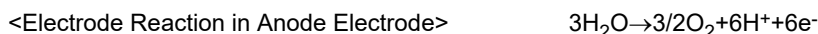
[0018] The catholyte LC is supplied to the cathode electrode 12 by the catholyte supply device 6. The catholyte LC contains an organic hydride raw material (substance to be hydrogenated) to be supplied to the cathode electrode 12. As an example, the catholyte LC does not contain an organic hydride before 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.

[0019] 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.

[0020] 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, and diphenylethane. 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.

[0021] 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 pyridine, pyrimidine, pyrazine, 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 piperidine.

[0022] 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).



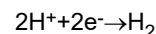
[0023] That is, the electrode reaction in the anode electrode 10 and the electrode reaction in the cathode electrode 12 proceed in parallel. The protons generated by electrolysis of water in the anode electrode 10 are supplied to the cathode electrode 12 through the membrane 14. Electrons generated by electrolysis of water are supplied to the cathode electrode 12 via an external circuit. The protons and electrons supplied to the cathode electrode 12 are used for the hydrogenation of toluene in the cathode electrode 12. As a result, methylcyclohexane is generated.

[0024] Therefore, according to the organic hydride production system 1 according to the present embodiment, the electrolysis of water 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.

[0025] In the cathode electrode 12, the following hydrogen gas generation reaction may occur as a side reaction together with the hydrogenation reaction of the substance to be hydrogenated which is the main reaction. As the supply amount of the substance to be hydrogenated to the cathode electrode 12 becomes insufficient, this side reaction is likely to occur.

<Side Reaction That Can Occur in Cathode Electrode>



[0026] When the protons move from the side of the anode electrode 10 to the side of the cathode electrode 12 through the membrane 14, the protons move together with water molecules. Therefore, water is accumulated in the cathode electrode 12 as the electrolytic reduction reaction proceeds.

[0027] The organic hydride production apparatus 2 is supplied with power from an external power supply (not shown). When power is supplied from the power supply to the organic hydride production apparatus 2, a predetermined electrolytic current is applied between the anode electrode 10 and the cathode electrode 12 of the organic hydride production apparatus 2, and an electrolytic current flows. The power supply sends power supplied from a power supply device to the organic hydride production apparatus 2. The power supply device can include 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 the power generation device using renewable energy, 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. In addition, a combination of two or more of them may be used.

[0028] The anolyte supply device 4 includes an anolyte tank 16, a first anode pipe 18, a second anode pipe 20, and an anode pump 22. The anolyte LA is stored in the anolyte tank 16. The anolyte tank 16 is connected to the anode electrode 10 by the first anode pipe 18. The anode pump 22 is provided in the middle of the first anode pipe 18. The anode pump 22 can include known pumps such as a gear pump and a cylinder pump. Note that the anolyte supply device 4 may circulate the anolyte LA using a liquid feeding device other than the pump. The anolyte tank 16 is connected to the anode electrode 10 by the second anode pipe 20.

[0029] The anolyte LA in the anolyte tank 16 flows into the anode electrode 10 through the first anode pipe 18 by driving of the anode pump 22. The anolyte LA flowing into the anode electrode 10 is subjected to an electrode reaction in the anode electrode 10. The anolyte LA in the anode electrode 10 is returned to the anolyte tank 16 through the second anode pipe 20. As an example, the anolyte tank 16 also functions as a gas-liquid separator. In the anode electrode 10, oxygen gas is generated by the electrode reaction. Therefore, the oxygen gas is mixed into the anolyte LA discharged from the anode electrode 10. The anolyte tank 16 separates the oxygen gas in the anolyte LA from the anolyte LA and discharges the oxygen gas to the outside of the system.

[0030] In the anolyte supply device 4 of the present embodiment, the anolyte LA is circulated between the anode electrode 10 and the anolyte tank 16. However, the present invention is not limited to this configuration, and the anolyte LA may be sent from the anode electrode 10 to the outside of the system without being returned to the anolyte tank 16.

[0031] The catholyte supply device 6 includes a catholyte tank 24, a first cathode pipe 26, a second cathode pipe 28, a third cathode pipe 30, a cathode pump 32, and a separator 34. The catholyte LC is stored in the catholyte tank 24. The catholyte tank 24 is connected to the cathode electrode 12 by the first cathode pipe 26. The cathode pump 32 is provided in the middle of the first cathode pipe 26. The cathode pump 32 can include known pumps such as a gear pump and a cylinder pump. Note that the catholyte supply device 6 may circulate the catholyte LC using a liquid feeding device other than the pump.

[0032] The separator 34 is connected to the cathode electrode 12 by the second cathode pipe 28. The separator 34 includes a known gas-liquid separator and a known oil-water separator. The separator 34 is connected to the catholyte tank 24 by the third cathode pipe 30.

[0033] The catholyte LC in the catholyte tank 24 flows into the cathode electrode 12 through the first cathode pipe 26 by driving of the cathode pump 32. The catholyte LC flowing into the cathode electrode 12 is subjected to an electrode reaction in the cathode electrode 12. The catholyte LC in the cathode electrode 12 flows into the separator 34 through the second cathode pipe 28. The hydrogen gas may be generated by the side reaction in the cathode electrode 12. Therefore, the hydrogen gas may be mixed in the catholyte LC discharged from the cathode electrode 12. The separator 34 separates the hydrogen gas in the catholyte LC from the catholyte LC and discharges the hydrogen gas to the outside of the system. In addition, water moves from the anode electrode 10 to the cathode electrode 12 together with protons. Therefore, the water may be mixed in the catholyte LC discharged from the cathode electrode 12. The separator 34 separates the water in the catholyte LC from the catholyte LC and discharges the water to the outside of the system. The catholyte LC from which the hydrogen gas and the water have been separated is returned to the catholyte tank 24 through the third cathode pipe 30.

[0034] In the catholyte supply device 6 of the present embodiment, the catholyte LC is circulated between the cathode electrode 12 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 12 without being returned to the catholyte tank 24.

[0035] Next, a structure of the organic hydride production apparatus 2 will be described in detail. Fig. 2 is a cross-sectional view of the organic hydride production apparatus 2. Fig. 3 is a cross-sectional view taken along the line A-A of Fig. 2. Fig. 4 is a schematic diagram of the membrane electrode assembly 8 and a cathode flow path 38 viewed from a lamination direction of the electrodes and the membrane. The organic hydride production apparatus 2 of the present embodiment includes an anode flow path 36 (anode flow path formation structure), a cathode flow path 38 (cathode flow path formation structure), a pair of plate members 42a and 42b, a gasket 44, and a flow obstruction member 46, in addition to the membrane electrode assembly 8.

[0036] The plate member 42a and the plate member 42b are made of a metal such as stainless steel or titanium, for example. The plate member 42a is laminated on the membrane electrode assembly 8 from the side of the anode electrode 10. The plate member 42b is laminated on the membrane electrode assembly 8 from the side of the cathode electrode 12. Accordingly, the membrane electrode assembly 8 is sandwiched between the pair of plate members 42a and 42b. A gap between the pair of plate members 42a and 42b is sealed with the gasket 44. When the organic hydride production system 1 includes only one organic hydride production apparatus 2, the pair of plate members 42a and 42b can correspond to a so-called end plate. When the organic hydride production system 1 includes a plurality of organic hydride production apparatuses 2, and another organic hydride production apparatus 2 is arranged next to the plate member 42a or the plate member 42b, the plate member can correspond to a so-called separator.

[0037] The cathode electrode 12 has a catalyst layer 12a and a diffusion layer 12b. The catalyst layer 12a is disposed closer to the membrane 14 than the diffusion layer 12b. The catalyst layer 12a is in contact with a main surface of the membrane 14. The catalyst layer 12a contains the cathode catalyst, the catalyst support, and the ionomer described above. The diffusion layer 12b is in contact with a main surface of the catalyst layer 12a on a side opposite to the membrane 14. The diffusion layer 12b uniformly diffuses the catholyte LC supplied from the outside into the catalyst layer 12a. The organic hydride generated in the catalyst layer 12a is discharged to the outside of the cathode electrode 12 through the diffusion layer 12b. The diffusion layer 12b includes a conductive material such as carbon or a metal. In addition, the diffusion layer 12b 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 12b include a carbon woven fabric (carbon cloth), a carbon nonwoven fabric, and carbon paper. Note that the diffusion layer 12b may be omitted.

[0038] The anode flow path 36 is connected to the anode electrode 10. The anode flow path 36 feeds and discharges the anolyte LA to and from the anode electrode 10. In the plate member 42a of the present embodiment, a groove is provided on a main surface facing the anode electrode 10 side. This groove forms the anode flow path 36. The anode flow path 36 covers an entire surface of the anode electrode 10, for example. The first anode pipe 18 and the second anode pipe 20 are connected to the anode flow path 36. As an example, the first anode pipe 18 is connected to a lower end of the anode flow path 36, and the second anode pipe 20 is connected to an upper end of the anode flow path 36. The connection positions of the first anode pipe 18 and the second anode pipe 20 with respect to the anode flow path 36 can be appropriately changed. By using the groove provided in the plate member 42a as the anode flow path 36, it is possible to suppress an increase in the number of parts due to the provision of the anode flow path 36, complication of the assembly process, and the like.

[0039] The cathode flow path 38 is connected to the cathode electrode 12. The cathode flow path 38 feeds and discharges the catholyte LC to and from the cathode electrode 12. In the plate member 42b of the present embodiment, a groove is provided on a main surface facing the cathode electrode 12 side. This groove forms the cathode flow path 38. The first cathode pipe 26 and the second cathode pipe 28 are connected to the cathode flow path 38. By using the groove provided in the plate member 42b as the cathode flow path 38, it is possible to suppress an increase in the number of parts due to the provision of the cathode flow path 38, complication of the assembly process, and the like.

[0040] The cathode flow path 38 of the present embodiment includes a supply flow path 38a (supply flow path formation structure) for supplying the catholyte LC to the cathode electrode 12, and a collection flow path 38b (collection flow path formation structure) for collecting the catholyte LC from the cathode electrode 12. The supply flow path 38a and the collection flow path 38b extend in the vertical direction, and side surfaces thereof face the cathode electrode 12. Note that "extending in the vertical direction" means that one end of a substantially linear flow path is positioned above the other end. Therefore, each flow path may extend obliquely with respect to a horizontal plane. The supply flow path 38a is disposed near one end of the plate member 42b in a horizontal direction, and the collection flow path 38b is disposed near the other end of the plate member 42b in the horizontal direction. The first cathode pipe 26 is connected to a lower end of the supply flow path 38a, and the second cathode pipe 28 is connected to an upper end of the collection flow path 38b. At least partial regions of the supply flow path 38a and the collection flow path 38b overlap each other when viewed from the horizontal direction. Preferably, the height positions of the lower ends of the respective flow paths are matched with each other, and the height positions of the upper ends of the respective flow paths are matched with each other.

[0041] The catholyte LC flowing into the supply flow path 38a from the first cathode pipe 26 flows from the lower side to the upper side in the supply flow path 38a, and is sent to the cathode electrode 12 from the side surface of the supply flow path 38a. The catholyte LC flowing into the cathode electrode 12 moves toward the collection flow path 38b in the cathode electrode 12. The catholyte LC that has reached the collection flow path 38b flows into the collection flow path 38b from the

cathode electrode 12. The catholyte LC flows into the supply flow path 38a from the side surface of the supply flow path 38a. Then, the catholyte LC flows from the lower side to the upper side in the collection flow path 38b and is discharged to the second cathode pipe 28. Note that the connection positions of the first cathode pipe 26 and the second cathode pipe 28 with respect to the cathode flow path 38 can be appropriately changed. For example, each pipe may be connected to a side surface rather than a bottom surface and a top surface of the cathode flow path 38. In addition, the number and arrangement of the supply flow path 38a and the collection flow path 38b can be appropriately changed.

[0042] The cathode electrode 12, the supply flow path 38a, and the collection flow path 38b have different ease of flow of the catholyte LC as follows. That is, when a flow resistance of the catholyte LC flowing through the cathode electrode 12 is R_1 , a flow resistance of the catholyte LC flowing through the collection flow path 38b is R_2 , and a flow resistance of the catholyte LC flowing through the supply flow path 38a is R_3 , the flow resistances R_1 to R_3 satisfy a relation of $R_1 > R_2 > R_3$.

[0043] The cathode electrode 12 includes a catalyst layer 12a in which a catalyst and a catalyst support are assembled, and a diffusion layer 12b including a porous body. On the other hand, the supply flow path 38a and the collection flow path 38b are formed of grooves provided on the surface of the plate member 42b. Therefore, the flow resistance R_1 in the cathode electrode 12 is inevitably larger than the flow resistance R_2 in the collection flow path 38b and the flow resistance R_3 in the supply flow path 38a. In the organic hydride production apparatus 2 of the present embodiment, the flow resistance R_2 in the collection flow path 38b is larger than the flow resistance R_3 in the supply flow path 38a by the flow obstruction member 46. As a result, the relation of $R_1 > R_2 > R_3$ can be satisfied.

[0044] The flow obstruction member 46 is disposed at least in the collection flow path 38b. As a result, the flow resistance R_2 in the collection flow path 38b can be caused to be larger than the flow resistance R_3 in the supply flow path 38a. The flow obstruction member 46 as an example is an elongated body extending along the collection flow path 38b. As a result, the flow resistance R_2 in the collection flow path 38b can be more easily caused to be larger than the flow resistance R_3 in the supply flow path 38a. The flow obstruction member 46 of the present embodiment is formed of a coil. The coil is formed of a metal such as titanium or stainless steel, for example. The coil extends spirally from one end side to the other end side inside the collection flow path 38b. As a result, it is possible to increase the flow resistance R_2 in the collection flow path 38b while suppressing the circulation of the catholyte LC from being completely blocked by the flow obstruction member 46.

[0045] Fig. 5A is a schematic diagram showing a flow of the catholyte LC when the flow resistance R_2 in the collection flow path 38b is equal to the flow resistance R_3 in the supply flow path 38a. Fig. 5B is a schematic diagram showing a flow of the catholyte LC when the flow resistance R_2 in the collection flow path 38b is larger than the flow resistance R_3 in the supply flow path 38a.

[0046] Due to the hydraulic pressure of the catholyte LC in the supply flow path 38a, the catholyte LC hardly travels to the upper portion of the supply flow path 38a. Therefore, when the flow resistance R_2 in the collection flow path 38b is equal to the flow resistance R_3 in the supply flow path 38a, as shown in Fig. 5A, a pressure distribution is likely to occur in which the pressure of the catholyte LC is low (flow rate is slow) in the upper portion of the cathode electrode 12 and the pressure of the catholyte LC is high (flow rate is fast) in the lower portion of the cathode electrode 12. The "upper portion" is, for example, a region of 1/2, preferably, 1/3 from the upper end of the cathode electrode 12. The "lower portion" is, for example, a region of 1/2, preferably, 1/3 from the lower end of the cathode electrode 12. In particular, the organic hydride production apparatus 2 may be large with a height of 1000 mm to 2000 mm. When the height of the organic hydride production apparatus 2 increases, the pressure decrease of the catholyte LC in the upper portion of the cathode electrode 12 becomes more remarkable.

[0047] As described above, hydrogen gas may be generated by the side reaction in the cathode electrode 12. Since the specific gravity of the hydrogen gas is smaller than that of the catholyte LC, the hydrogen gas is likely to be accumulated in the upper portion of the cathode electrode 12. The hydrogen gas accumulated in the cathode electrode 12 is pushed out to the collection flow path 38b by the catholyte LC and discharged to the second cathode pipe 28. However, when the pressure of the catholyte LC is low in the upper portion of the cathode electrode 12, the hydrogen gas tends to remain. When a large amount of hydrogen gas is accumulated in the cathode electrode 12, the amount of the substance to be hydrogenated supplied to the reaction field of the catalyst layer 12a decreases, and the side reaction is more likely to proceed. The occurrence of the side reaction leads to reduction in the Faraday efficiency at the time of producing the organic hydride.

[0048] On the other hand, in the organic hydride production apparatus 2 of the present embodiment, the flow resistance R_2 in the collection flow path 38b is larger than the flow resistance R_3 in the supply flow path 38a. As a result, as shown in Fig. 5B, the movement of the catholyte LC toward the collection flow path 38b in the lower portion of the supply flow path 38a can be suppressed, and the catholyte LC can be guided to the upper portion of the supply flow path 38a. Therefore, the pressure of the catholyte LC in the upper portion of the cathode electrode 12 can be increased, and the hydrogen gas accumulated in the upper portion of the cathode electrode 12 can be more easily discharged. As a result, the electrolytic performance of the organic hydride production apparatus 2 can be improved.

[0049] In the present embodiment, the flow obstruction members 46 are disposed in both the supply flow path 38a and the collection flow path 38b. The flow obstruction member 46 disposed in the supply flow path 38a is formed of a coil having a relatively small wire diameter, and the flow obstruction member 46 disposed in the collection flow path 38b is formed of a

coil having a relatively large wire diameter. As a result, the flow resistance R2 in the collection flow path 38b can be caused to be larger than the flow resistance R3 in the supply flow path 38a.

[0050] As shown in Fig. 4, the cathode flow path 38 is disposed so as to overlap the membrane electrode assembly 8 when viewed from the lamination direction of the cathode electrode 12, the membrane 14, and the anode electrode 10.

Generally, in the organic hydride production apparatus, a high pressure is applied to the membrane electrode assembly to bring the layers into close contact with each other. Accordingly, the production efficiency of the organic hydride can be increased. The pressure applied to the membrane electrode assembly is larger than the pressure applied to a general fuel cell. For this reason, when the membrane electrode assembly 8 and the cathode flow path 38 overlap each other, the membrane electrode assembly 8 can be fitted into the cathode flow path 38. When the membrane electrode assembly 8 is fitted into the cathode flow path 38, a pressure loss generated in the catholyte LC flowing through the cathode flow path 38 may be excessively increased. The increase in the pressure loss is not intended. In addition, the cathode flow path 38 is blocked, the supply of the substance to be hydrogenated to the cathode electrode 12 is delayed, and the reaction for producing the organic hydride in at least a part of the cathode electrode 12 may be stopped. In addition, generation of hydrogen occurs due to the side reactions, and the Faraday efficiency during production of the organic hydride may be reduced.

[0051] On the other hand, by disposing the flow obstruction members 46 in the supply flow path 38a and the collection flow path 38b, the membrane electrode assembly 8 can be supported by the flow obstruction members 46. This makes it possible to suppress fitting of the membrane electrode assembly 8 into the cathode flow path 38. Therefore, the electrolytic performance of the organic hydride production apparatus 2 can be improved.

[0052] The collection flow path 38b is located at the downstream of the supply flow path 38a in the flow of the catholyte LC, and tends to have a lower internal pressure than the supply flow path 38a. For this reason, in the collection flow path 38b, the membrane electrode assembly 8 is easily fitted as compared with the supply flow path 38a. Therefore, the flow obstruction member 46 is preferably disposed at least in the collection flow path 38b. The difference between the flow resistance R2 and the flow resistance R3 can also be realized by providing the flow obstruction member 46 in the collection flow path 38b. On the other hand, when the driving of the cathode pump 32 is stopped and the supply of the catholyte LC to the cathode electrode 12 is stopped, the internal pressure of the supply flow path 38a may also decrease. Therefore, by disposing the flow obstruction members 46 in both the supply flow path 38a and the collection flow path 38b, the electrolytic performance of the organic hydride production apparatus 2 can be further improved.

(Modifications)

[0053] The organic hydride production apparatus 2 according to the above-described embodiment can include the following modifications. That is, the flow obstruction member 46 of the embodiment is formed of the coil, but is not particularly limited to this configuration. For example, the flow obstruction member 46 may be formed of a stent. The stent is a meshed tube. Therefore, the stent extends along the collection flow path 38b. The material of the stent is similar to that of the coil. The flow obstruction member 46 may be formed of a porous member having liquid permeability such as porous ceramics. The porous member may be an elongated body extending along the collection flow path 38b. By disposing the stent or the porous member in the collection flow path 38b, the flow resistance R2 in the collection flow path 38b can be caused to be larger than the flow resistance R3 in the supply flow path 38a, similarly to the case of the coil.

[0054] The stent or the porous member may also be provided in the supply flow path 38a. In this case, the flow resistance R2 in the collection flow path 38b can be caused to be larger than the flow resistance R3 in the supply flow path 38a by changing a diameter of a wire rod forming the stent or changing a porosity of the porous member. The collection flow path 38b and the supply flow path 38a may be different from each other in at least one of the width, depth, and shape of the flow path to provide a difference between the flow resistance R2 in the collection flow path 38b and the flow resistance R3 in the supply flow path 38a.

[0055] The embodiments may also be specified as items described below.

[First Item]

[0056] An organic hydride production apparatus (2) including:

- a membrane electrode assembly (8) in which an anode electrode (10) that oxidizes water in an anolyte (LA) to generate protons and a cathode electrode (12) that hydrogenates a substance to be hydrogenated in a catholyte (LC) with the protons to generate an organic hydride are laminated with a membrane (14) that moves the protons from an anode electrode (10) side to a cathode electrode (12) side interposed therebetween;
- a supply flow path (38a) which extends in a vertical direction, in which the catholyte (LC) flows from a lower side to an upper side, and through which the catholyte (LC) is sent to the cathode electrode (12); and
- a collection flow path (38b) which extends in the vertical direction and into which the catholyte (LC) flows from the

cathode electrode (12), wherein

a flow resistance R1 of the catholyte (LC) flowing through the cathode electrode (12), a flow resistance R2 of the catholyte (LC) flowing through the collection flow path (38b), and a flow resistance R3 of the catholyte (LC) flowing through the supply flow path (38a) satisfy a relation of $R1 > R2 > R3$.

[Second Item]

[0057] The organic hydride production apparatus (2) according to the first item, wherein

the organic hydride production apparatus (2) includes a plate member (42b) laminated on the membrane electrode assembly (8),

the supply flow path (38a) and the collection flow path (38b) are formed of grooves provided on a surface of the plate member (42b), and

the organic hydride production apparatus (2) includes a flow obstruction member (46) disposed at least in the collection flow path (38b) to increase the flow resistance R2 in the collection flow path (38b) to be larger than the flow resistance R3 in the supply flow path (38a).

[Third Item]

[0058] The organic hydride production apparatus (2) according to the second item, wherein the flow obstruction member (46) is an elongated body extending along the collection flow path (38b).

[Fourth Item]

[0059] The organic hydride production apparatus (2) according to the third item, wherein the flow obstruction member (46) is formed of a coil or a stent.

[Fifth Item]

[0060] The organic hydride production apparatus (2) according to the second item or the third item, wherein the flow obstruction member (46) is formed of a porous member.

Examples

[0061] Hereinafter, examples of the present invention will be described, but these examples are merely examples for suitably describing the present invention, and do not limit the present invention at all.

(Example 1)

[0062] An organic hydride production apparatus was prepared in which the flow obstruction member was disposed in the collection flow path and not disposed in the supply flow path. A coil having a wire diameter ϕ of 0.6 mm was used as the flow obstruction member. The flow obstruction member was provided only in the collection flow path, so that the flow resistance R1 in the cathode electrode, the flow resistance R2 in the collection flow path, and the flow resistance R3 in the supply flow path satisfied $R1 > R2 > R3$.

[0063] A difference between the pressure of the catholyte at a position in contact with the supply flow path and the pressure of the catholyte at a position in contact with the collection flow path was measured at four positions of a lower portion, an intermediate lower portion, an intermediate upper portion, and an upper portion of the cathode electrode. The lower portion is located approximately at the lower end of the cathode electrode, the intermediate lower portion is located at about 1/3 of the height of the cathode electrode, the intermediate upper portion is located at about 2/3 of the height of the cathode electrode, and the upper portion is located approximately at the upper end of the cathode electrode.

[0064] A catholyte having a toluene concentration of 100% was circulated through the cathode electrode of the organic hydride production apparatus. In addition, an aqueous sulfuric acid solution was circulated as an anolyte to the anode electrode. Then, an electrolytic reaction was performed at a current density of 0.6 A/cm². The electrolytic reaction was performed until the Faraday efficiency converted from the production amount of by-product hydrogen reached 95%. When hydrogen in an amount corresponding to the Faraday efficiency of 95% was generated, the catholyte was collected at the inlet of the cathode flow path, and the toluene concentration of the catholyte was measured using a gas chromatograph. The results are shown in Fig. 6. This toluene concentration corresponds to the electrolytic performance of the organic hydride production apparatus. This means that the electrolysis performance is higher when the toluene concentration is

lower.

(Example 2)

- 5 **[0065]** An organic hydride production apparatus having the same configuration as Example 1 except that a coil having a wire diameter ϕ of 0.1 mm was disposed in the supply flow path was prepared. A flow obstruction member having a larger wire diameter than the flow obstruction member provided in the supply flow path was provided in the collection flow path, so that the flow resistance R1 in the cathode electrode, the flow resistance R2 in the collection flow path, and the flow resistance R3 in the supply flow path satisfied $R1 > R2 > R3$. Then, a differential pressure in the cathode electrode was measured similarly to Example 1. The electrolytic reaction was performed under the same conditions as Example 1, and the toluene concentration of the catholyte at the Faraday efficiency of 95% was measured. The results are shown in Fig. 6.

(Comparative Example 1)

- 15 **[0066]** An organic hydride production apparatus having the same configuration as Example 1 except that the flow obstruction member was not disposed in the collection flow path was prepared. The flow obstruction members were not provided in both the collection flow path and the supply flow path, so that the flow resistance R1 in the cathode electrode, the flow resistance R2 in the collection flow path, and the flow resistance R3 in the supply flow path satisfied $R1 > R2 = R3$. Then, a differential pressure in the cathode electrode was measured similarly to Example 1. The electrolytic reaction was performed under the same conditions as Example 1, and the toluene concentration of the catholyte at the Faraday efficiency of 95% was measured. The results are shown in Fig. 6.

(Comparative Example 2)

- 25 **[0067]** An organic hydride production apparatus having the same configuration as Example 1 except that a coil having a wire diameter ϕ of 0.6 mm was disposed in both the collection flow path and the supply flow path was prepared. The flow obstruction members having the same wire diameter were provided in both the collection flow path and the supply flow path, so that the flow resistance R1 in the cathode electrode, the flow resistance R2 in the collection flow path, and the flow resistance R3 in the supply flow path satisfied $R1 > R2 = R3$. Then, a differential pressure in the cathode electrode was measured similarly to Example 1. The electrolytic reaction was performed under the same conditions as Example 1, and the toluene concentration of the catholyte at the Faraday efficiency of 95% was measured. The results are shown in Fig. 6.
- 30 **[0068]** Fig. 6 is a diagram showing the differential pressure in the cathode electrode and the toluene concentration at the Faraday efficiency (F efficiency) of 95% in each organic hydride production apparatus of each Example and each Comparative Example. As shown in Fig. 6, in Examples 1 and 2 in which the flow resistance R2 of the collection flow path was larger than the flow resistance R3 of the supply flow path, the differential pressure of the catholyte in the upper portion of the cathode electrode was larger than the differential pressure in the lower portion or the intermediate lower portion. This means that more catholyte could be guided to the upper portion of the supply flow path. On the other hand, in Comparative Examples 1 and 2 in which the flow resistance R2 of the collection flow path and the flow resistance R3 of the supply flow path were equal to each other, the differential pressure of the catholyte in the upper portion of the cathode electrode was lower than the differential pressure in the lower portion or the intermediate lower portion.

- 35 **[0069]** In Examples 1 and 2, the toluene concentration at the Faraday efficiency of 95% was lower than that in Comparative Examples 1 and 2. From the above results, it was confirmed that the electrolytic performance of the organic hydride production apparatus was improved by adjusting the flow resistance R1 in the cathode electrode, the flow resistance R2 in the collection flow path, and the flow resistance R3 in the supply flow path so as to satisfy $R1 > R2 > R3$.

INDUSTRIAL APPLICABILITY

[0070] The present invention can be used in an organic hydride production apparatus.

REFERENCE SIGNS LIST

[0071] 2 organic hydride production apparatus, 8 membrane electrode assembly, 10 anode electrode, 12 cathode electrode, 14 membrane, 38a supply flow path, 38b collection flow path, 42b plate member, 46 flow obstruction member, R1, R2, R3 flow resistance

Claims

1. An organic hydride production apparatus comprising:

5 a membrane electrode assembly in which an anode electrode that oxidizes water in an anolyte to generate protons and a cathode electrode that hydrogenates a substance to be hydrogenated in a catholyte with the protons to generate an organic hydride are laminated with a membrane that moves the protons from the anode electrode side to the cathode electrode side interposed therebetween;
 10 a supply flow path which extends in a vertical direction, in which the catholyte flows from a lower side to an upper side, and through which the catholyte is sent to the cathode electrode; and
 a collection flow path which extends in the vertical direction and into which the catholyte flows from the cathode electrode, wherein
 a flow resistance R1 of the catholyte flowing through the cathode electrode, a flow resistance R2 of the catholyte flowing through the collection flow path, and a flow resistance R3 of the catholyte flowing through the supply flow path satisfy a relation of $R1 > R2 > R3$.
 15

2. The organic hydride production apparatus according to claim 1, wherein

20 the organic hydride production apparatus comprises a plate member laminated on the membrane electrode assembly,
 the supply flow path and the collection flow path are formed of grooves provided on a surface of the plate member, and
 the organic hydride production apparatus comprises a flow obstruction member disposed at least in the collection flow path and structured to increase the flow resistance R2 in the collection flow path to be larger than the flow resistance R3 in the supply flow path.
 25

3. The organic hydride production apparatus according to claim 2, wherein the flow obstruction member is an elongated body extending along the collection flow path.

4. The organic hydride production apparatus according to claim 3, wherein the flow obstruction member is formed of a coil or a stent.

5. The organic hydride production apparatus according to claim 2 or 3, wherein the flow obstruction member is formed of a porous member.

FIG. 1

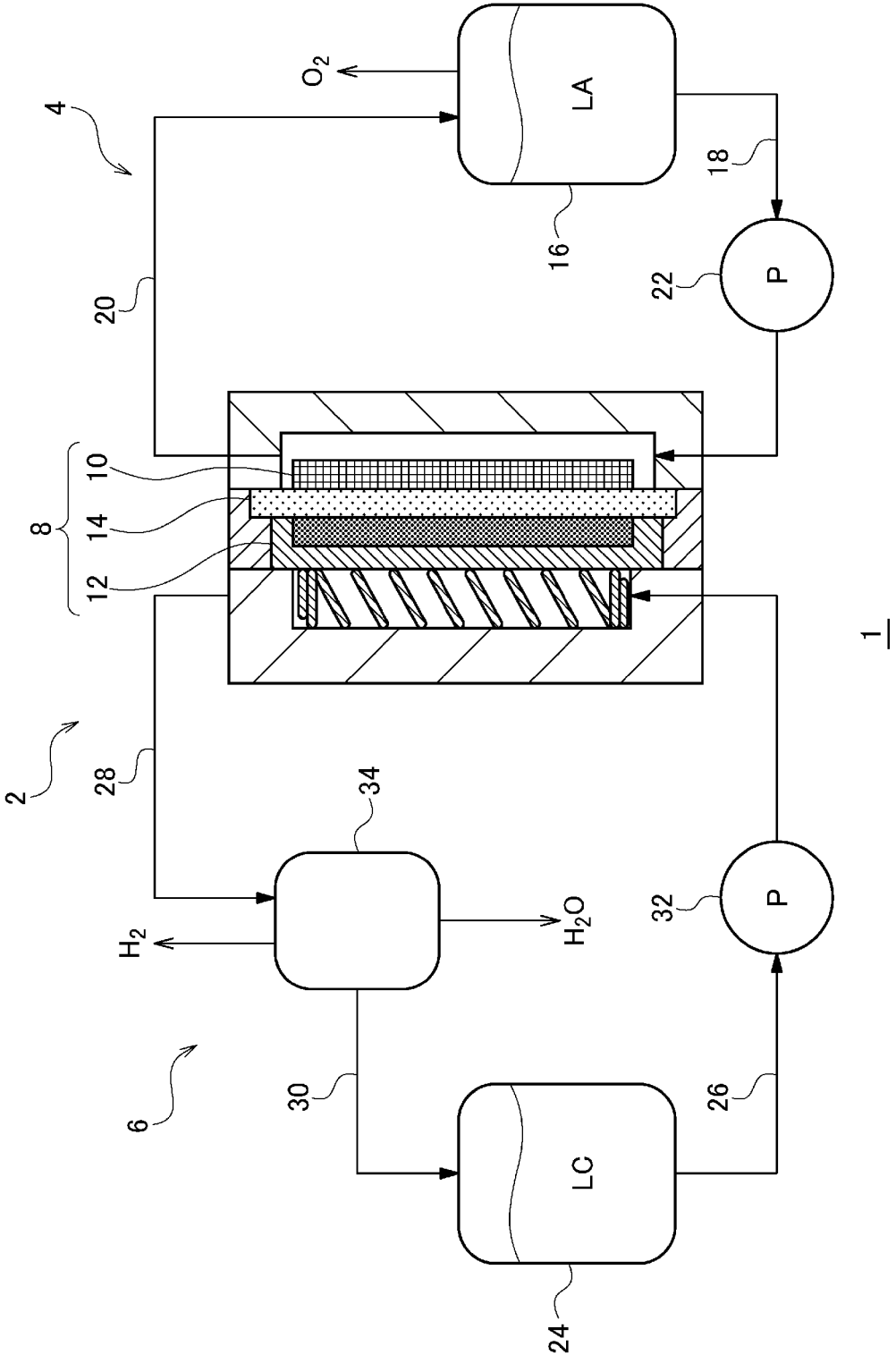


FIG. 2

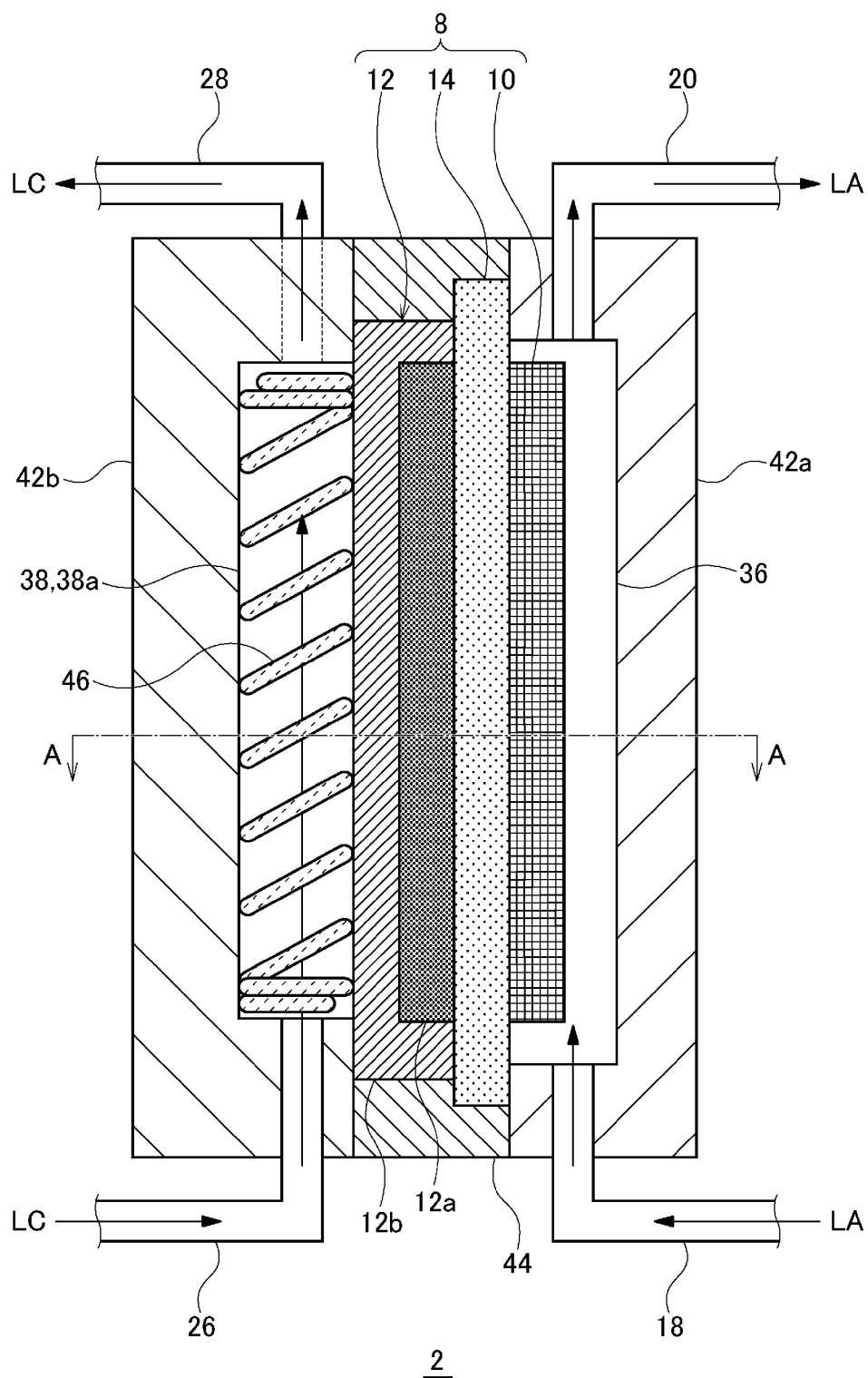


FIG. 3

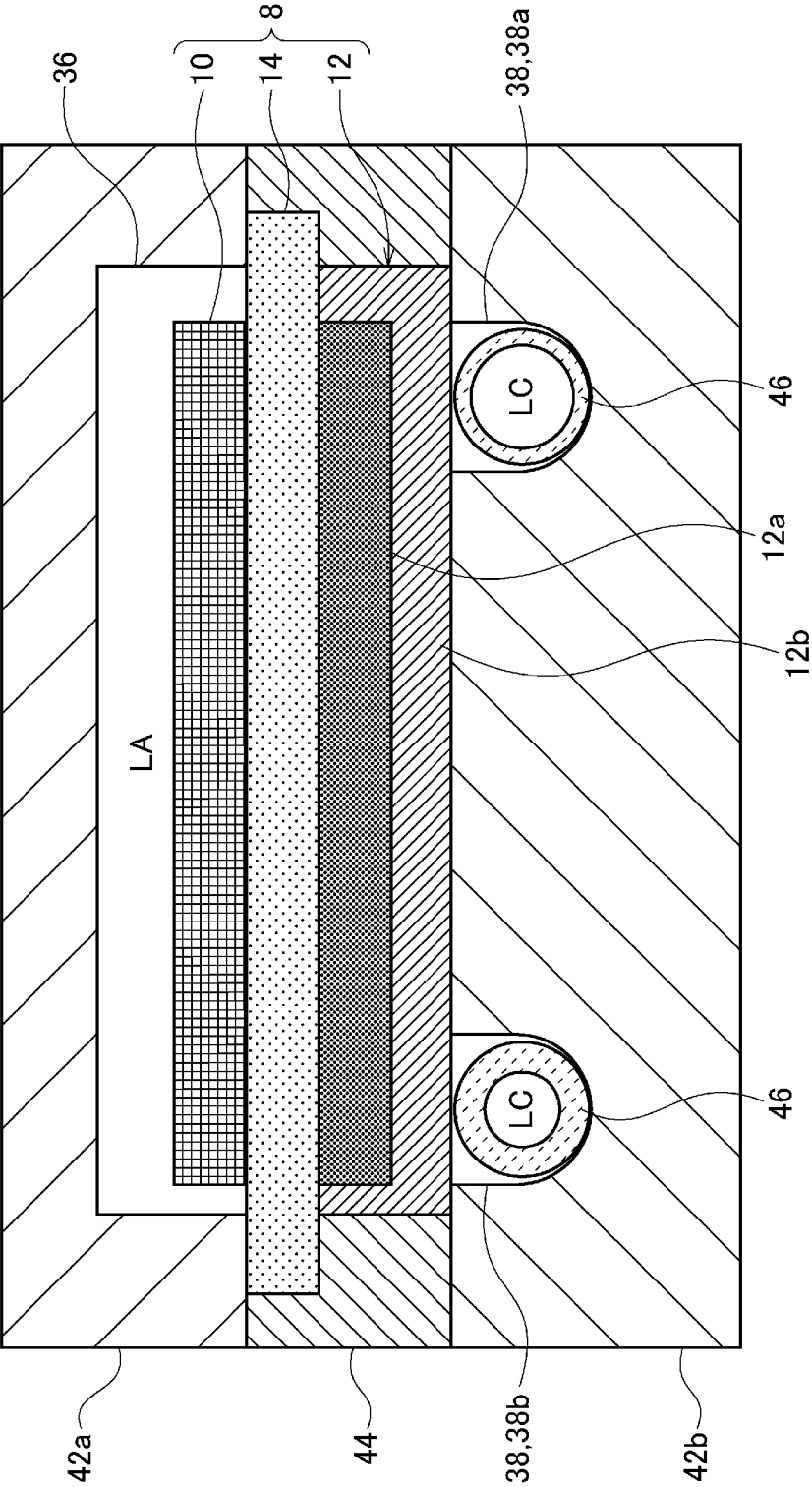


FIG. 4

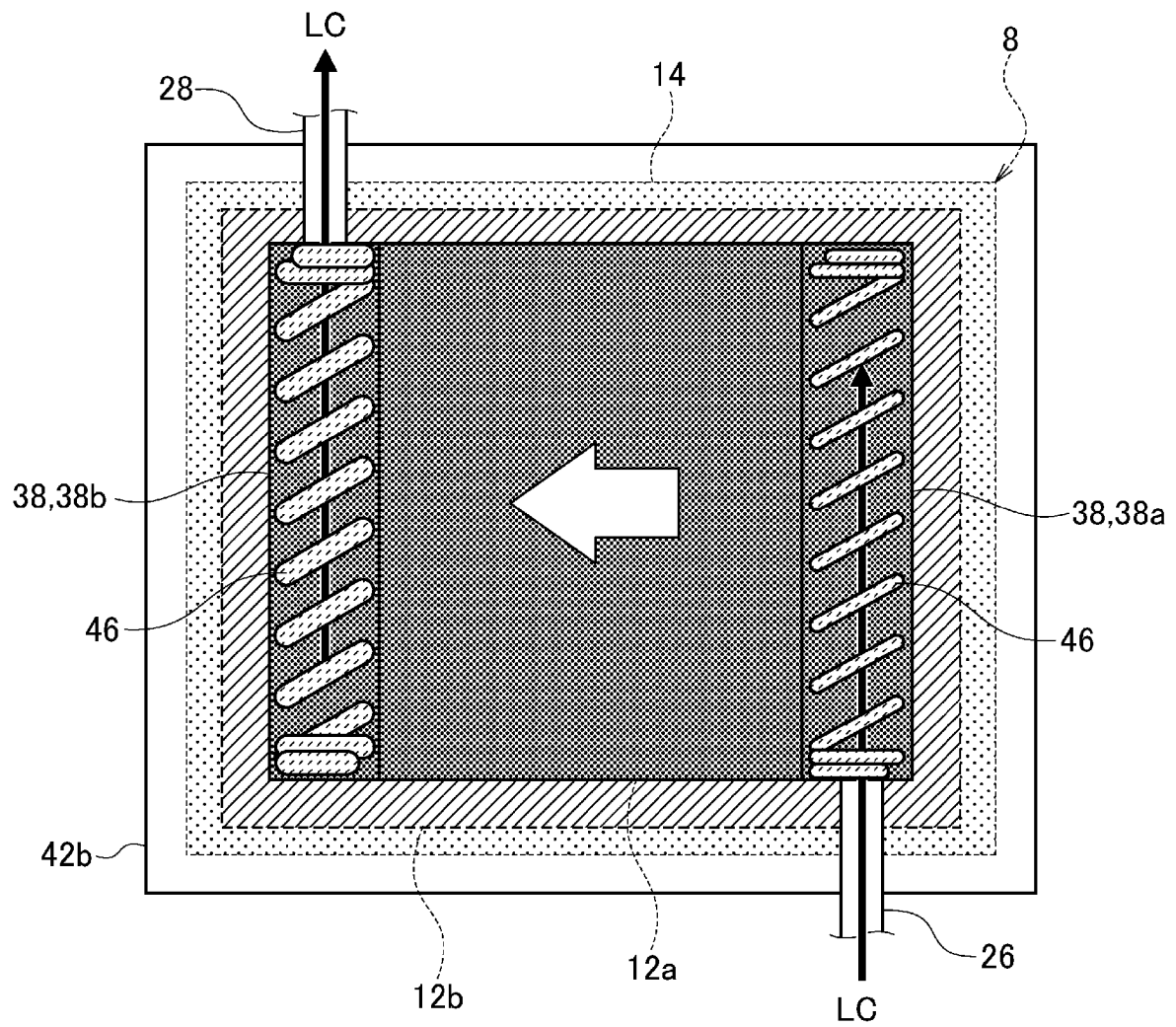


FIG. 5A

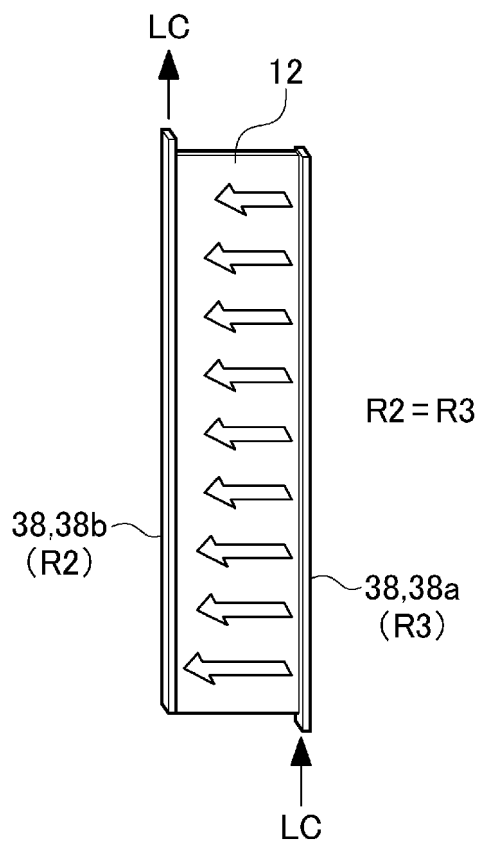


FIG. 5B

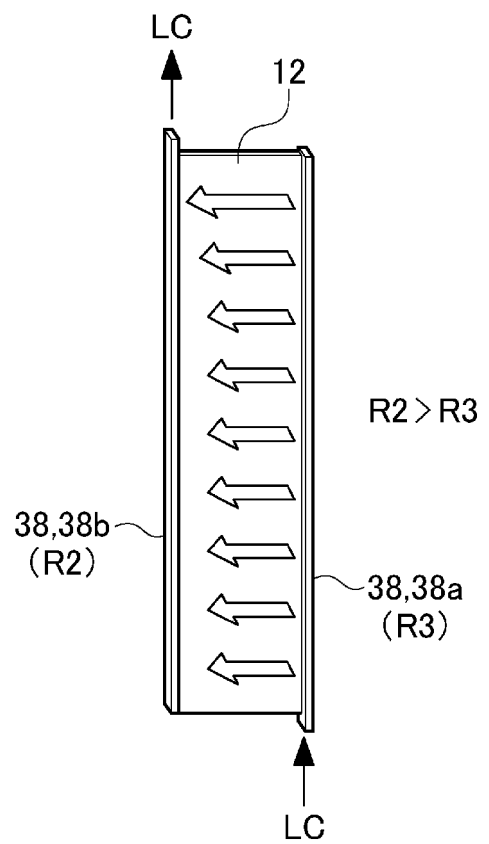


FIG. 6

	FLOW OBSTRUCTION MEMBER		DIFFERENTIAL PRESSURE IN CATHODE ELECTRODE (kPa)			TOLUENE CONCENTRATION AT F EFFICIENCY OF 95% (%)
	SUPPLY FLOW PATH	RECOVERY FLOW PATH	LOWER PORTION	INTERMEDIATE LOWER PORTION	INTERMEDIATE UPPER PORTION	
EXAMPLE 1	ABSENCE	PRESENCE WIRE DIA-METER $\phi 0.6$	17.3	16.3	20.0	12.2%
EXAMPLE 2	PRESENCE WIRE DIA-METER $\phi 0.1$	PRESENCE WIRE DIA-METER $\phi 0.6$	19.5	15.1	18.6	10.1%
COMPARATIVE EXAMPLE 1	ABSENCE	ABSENCE	23.2	21.4	19.9	13.6%
COMPARATIVE EXAMPLE 2	PRESENCE WIRE DIA-METER $\phi 0.6$	PRESENCE WIRE DIA-METER $\phi 0.6$	29.9	21.3	19.9	14.0%

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2023/004020

A. CLASSIFICATION OF SUBJECT MATTER

C25B 9/00(2021.01)i; *C25B 3/03*(2021.01)i; *C25B 3/25*(2021.01)i; *C25B 9/23*(2021.01)i; *C25B 9/60*(2021.01)i;
C25B 15/02(2021.01)i

FI: C25B9/00 G; C25B3/03; C25B3/25; C25B9/23; C25B9/60; C25B15/02

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)

C25B9/00; C25B3/03; C25B3/25; C25B9/23; C25B9/60; C25B15/02

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2021-109986 A (ENEOS CORP) 02 August 2021 (2021-08-02)	1-5
A	JP 2016-098410 A (NAT UNIV YOKOHAMA) 30 May 2016 (2016-05-30)	1-5
A	JP 2017-179601 A (JX NIPPON OIL & ENERGY CORP) 05 October 2017 (2017-10-05)	1-5

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

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“&” document member of the same patent family

Date of the actual completion of the international search

05 April 2023

Date of mailing of the international search report

18 April 2023

Name and mailing address of the ISA/JP

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2023/004020

Patent document cited in search report				Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
JP	2021-109986	A		02 August 2021	(Family: none)			
JP	2016-098410	A		30 May 2016	US	2017/0314145	A1	
					WO	2016/080505	A1	
					EP	3222754	A1	
					CA	2968036	A	
					KR	10-2017-0085591	A	
					CN	107075700	A	
					DK	3222754	T	
					ES	2846853	T	
JP	2017-179601	A		05 October 2017	(Family: none)			

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

REFERENCES CITED IN THE DESCRIPTION

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