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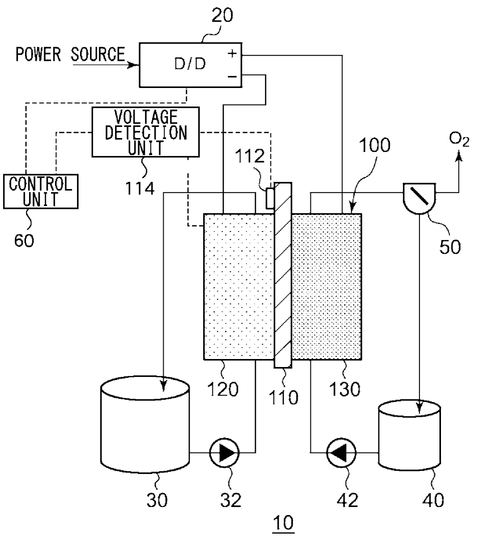
(54) ELECTROCHEMICAL REDUCTION DEVICE, AND METHOD FOR PRODUCING HYDROGENATED PRODUCT OF AROMATIC HYDROCARBON COMPOUND OR NITROGEN-CONTAINING HETEROCYCLIC AROMATIC COMPOUND

(57) An electrochemical reduction device 10 is provided with an electrode unit 100, a power control unit 20, an organic material storage tank 30, a water storage tank 40, a gas-liquid separator 50, and a control unit 60. The electrode unit 100 has an electrolyte membrane 110, a reduction electrode 120, and an oxygen evolving electrode 130. The electrolyte membrane 110 is formed of an ionomer. A reduction catalyst used for the reduction electrode 120 contains at least one of Pt and Pd. The oxygen evolving electrode 130 contains catalysts of noble metal oxides such as RuO_2, IrO_2, and the like. The control unit 60 controls the power control unit 20 such that a relationship, V_{HER} - 20 mV ≤ V_{CA} - V_{TRR}, can be satisfied when the potential at a reversible hydrogen electrode, the standard redox potential of an aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound, and the potential of the reduction electrode 120 are expressed as V_{HER}, V_{TRR}, and V_{CA}, respectively.

FIG.1



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Description

[TECHNICAL FIELD]

[0001] The present invention relates to a device and a method for electrochemically hydrogenating an aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound.

[BACKGROUND ART]

[0002] It is known that cyclic organic compounds such as cyclohexane and decalin are able to be obtained efficiently by hydrogenating a benzene ring of corresponding aromatic hydrocarbon compounds (benzene and naphthalene) using a hydrogen gas. Since high temperature and high pressure are required for this reaction, this reaction is not suitable for small and medium-scale manufacturing. On the other hand, in the case of an electrochemical reaction where an electrolysis cell is used, it is not necessary to treat gaseous hydrogen since water can be used as a source of hydrogen, and the reaction is known to progress under relatively mild reaction conditions (at about room temperature to 200°C and under normal pressure).

[prior art document]

[patent document]

[0003]

[Patent document No. 1] JP 2003-045449
[Patent document No. 2] JP 2005-126288
[Patent Document No. 3] JP 2005-239479

[non-patent document]

[0004] [non-patent document No. 1] Masaru Ichikawa, J. Jpn. Inst. Energy, vol. 85, 517 (2006)

[DISCLOSURE OF THE INVENTION]

[PROBLEM TO BE SOLVED BY THE INVENTION]

[0005] As an example for electrochemically hydrogenating a benzene ring of an aromatic hydrocarbon compound such as toluene or the like, a method has been reported for obtaining methylcyclohexane, which is a hydride in which a benzene ring is hydrogenated, without going through a state of a hydrogen gas by sending toluene that is vaporized into a gaseous state to the side of a reduction electrode in a configuration similar to that of water electrolysis (see non-patent document No. 1). However, the amount of substance (current density) that can be transformed per electrode area and time is not large, and it has been difficult to industrially hydrogenate a benzene ring of aromatic hydrocarbon compounds.

[0006] In this background, a purpose of the present invention is to provide a technology capable of electrochemically hydrogenating at least one benzene ring of an aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound with high efficiency.

[0007] One embodiment of the present invention relates to an electrochemical reduction device. The electrochemical reduction device includes: an electrode unit including an electrolyte membrane having ionic conductivity, a reduction electrode that is provided on one side of the electrolyte membrane and that contains a reduction catalyst for hydrogenating at least one benzene ring of an aromatic hydrocarbon compound, and an oxygen evolving electrode that is provided on the other side of the electrolyte membrane; a power control unit that applies a voltage Va between the reduction electrode and the oxygen evolving electrode; and a control unit that controls the power control unit such that a relationship, V_{HER} - arbitrarily-defined acceptable potential $\leq V_{CA} \leq V_{TRR}$, can be satisfied when the potential at a reversible hydrogen electrode, the standard redox potential of the aromatic hydrocarbon compound, and the potential of the reduction electrode are expressed as V_{HER}, V_{TRR}, and V_{CA}, respectively. A potential in the present invention means a true electrode potential with respect to a reference potential. Therefore, when there exist, for example, an electrolyte membrane resistance, an electrode catalyst layer resistance, an ohmic loss derived from various electrical connections, and the like, a true electrode potential needs to be calculated and/or corrected in consideration of these as described later.

[0008] In the electrochemical reduction device according to the above embodiment, the arbitrarily-defined acceptable potential may be 20 mV. The electrochemical reduction device may further include: a reference electrode that is arranged to be in contact with the electrolyte membrane and to be electrically isolated from the reduction electrode and the oxygen evolving electrode and that is held at a reference electrode potential V_{Ref}; and a voltage detection unit that detects a potential difference ΔV_{CA} between the reference electrode and the reduction electrode, and the control unit may acquire the potential V_{CA} of the reduction electrode based on the potential difference ΔV_{CA} and the reference electrode potential V_{Ref}. The control unit may control the potential V_{CA} of the reduction electrode to be in a predetermined range by changing the voltage Va. When an oxygen evolution equilibrium potential in the electrolysis of water is expressed as V_{OER}, the control unit controls the power control unit such that an expression, $Va \geq (V_{OER} - V_{CA})$, is satisfied. The reference electrode may be arranged on the side of the electrolyte membrane on which the reduction electrode is provided.

[0009] Another embodiment of the present invention relates to an electrochemical reduction device. The electrochemical reduction device includes: an electrode unit assembly in which a plurality of electrode units are electrically connected to one another in series, the electrode units each including an electrolyte membrane having ionic conductivity, a reduction electrode that is provided on one side of the electrolyte membrane and that contains a reduction catalyst for hydrogenating at least one benzene ring of an aromatic hydrocarbon compound, and an oxygen evolving electrode that is provided on the other side of the electrolyte membrane; a power control unit that applies a voltage VA between a positive electrode terminal and a negative electrode terminal of the electrode unit assembly; and a control unit that controls the power control unit such that a relationship, V_{HER} - arbitrarily-defined acceptable potential $\leq V_{CA} \leq V_{TRR}$, can be satisfied when the potential at a reversible hydrogen electrode, the standard redox potential of the aromatic hydrocarbon compound, and the potential of the reduction electrode of each electrode unit are expressed as V_{HER}, V_{TRR}, and V_{CA}, respectively.

[0010] In the electrochemical reduction device according to the above embodiment, the arbitrarily-defined acceptable potential may be 20 mV. The electrochemical reduction device may further include: a reference electrode that is arranged to be in contact with an electrolyte membrane of any one of electrolytic layers contained in the electrode unit assembly and to be electrically isolated from the reduction electrode and the oxygen evolving electrode; and a voltage detection unit that detects a potential difference ΔV_{CA} between the reference electrode and the reduction electrode, and the control unit may acquire the potential V_{CA} of the reduction electrode based on the potential difference ΔV_{CA} and the reference electrode potential V_{Ref}. The control unit may control the potential V_{CA} of the reduction electrode of each electrode unit to be in a predetermined range by changing the voltage VA. When an oxygen evolution equilibrium potential in the electrolysis of water is expressed as V_{OER}, the control unit may control the power control unit such that an expression, $Va \geq (V_{OER} - V_{CA}) \times N$, is satisfied where N (two or greater) is the number of serially-concatenated electrode units. The reference electrode may be arranged on the side of the electrolyte membrane on which the reduction electrode is provided. The reference electrode may be arranged on the side of the electrolyte membrane on which the reduction electrode is provided.

[0011] Another embodiment of the present invention relates to a method for manufacturing a hydride of an aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound. The method for manufacturing a hydride of an aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound includes introducing an aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound to the reduction electrode side of the electrode unit, circulating water or a humidified gas to the oxygen evolving electrode side, and hydrogenating at least one benzene ring of the aromatic hydrocarbon compound or the N-containing heterocyclic aromatic compound introduced to the reduction electrode side, by using the electrochemical reduction device according to any one of above-stated embodiments. In the method for manufacturing a hydride of an aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound according to the embodiment, the aromatic hydrocarbon compound or the N-containing heterocyclic aromatic compound to be introduced to the reduction electrode side may be introduced to the reduction electrode side in a liquid state at a reaction temperature.

[0012] Combinations of the above-stated elements will also be within the scope of the present invention sought to be patented by the present patent application.

[ADVANTAGE OF THE INVENTION]

[0013] According to the present invention, at least one benzene ring of an aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound can be electrochemically hydrogenated with high efficiency.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0014]

Fig. 1 is a schematic diagram illustrating the configuration of an electrochemical reduction device according to a first embodiment;

Fig. 2 is a diagram illustrating the configuration of an electrode unit of the electrochemical reduction device according to the first embodiment;

Fig. 3 is a flowchart illustrating an example of potential control of a reduction electrode by a control unit;

Fig. 4 is a graph illustrating a relationship between the potential of the reduction electrode and various types of current density;

Fig. 5 is a schematic diagram illustrating the configuration of an electrochemical reduction device according to a second embodiment; and

Fig. 6 is a schematic diagram illustrating the configuration of an electrochemical reduction device according to a third embodiment.

[BEST MODE FOR CARRYING OUT THE INVENTION]

[0015] Described below is an explanation of the embodiments of the present invention with reference to figures. In the figures, like numerals represent like constituting elements, and the description thereof is omitted appropriately.

(First Embodiment)

[0016] Fig. 1 is a schematic diagram illustrating the configuration of an electrochemical reduction device 10 according to an embodiment. Fig. 2 is a diagram illustrating the configuration of an electrode unit of the electrochemical reduction device 10 according to the embodiment. As shown in Fig. 1, the electrochemical reduction device 10 has an electrode unit 100, a power control unit 20, an organic material storage tank 30, a water storage tank 40, a gas-liquid separator 50, and a control unit 60.

[0017] The power control unit 20 is, for example, a DC/DC converter for converting the output voltage of a power source into a predetermined voltage. The positive electrode output terminal of the power control unit 20 is connected to the positive electrode of the electrode unit 100. The negative electrode output terminal of the power control unit 20 is connected to the negative electrode of the electrode unit 100. With this, a predetermined voltage is applied between an oxygen evolving electrode (positive electrode) 130 of the electrode unit 100 and a reduction electrode (negative electrode) 120. A reference electrode input terminal of the power control unit 20 is connected to a reference electrode 112 provided on an electrolyte membrane 110, which will be described later, and the potential of the positive electrode output terminal and the potential of the negative electrode output terminal are determined based on the potential of the reference electrode 112 in accordance with an instruction from the control unit 60. As the power source, electrical power derived from natural energy such as sunlight, wind power, and the like can be used. The mode of the potential control of the positive electrode output terminal and the negative electrode output terminal by the control unit 60 will be described later.

[0018] The organic material storage tank 30 stores an aromatic compound. An aromatic compound used in the present embodiment is an aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound containing at least one aromatic ring and includes benzene, naphthalene, anthracene, diphenylethane, pyridine, pyrimidine, pyrazine, quinoline, isoquinoline, N-alkylpyrrole, N-alkylindole, N-alkyldibenzopyrrole and the like. One through four hydrogen atoms of the aromatic ring of the aromatic hydrocarbon compound or the N-containing heterocyclic aromatic compound may be substituted by alkyl groups. An "alkyl" of the above aromatic compounds is a linear or branched alkyl group with one through six carbons. For example, alkylbenzene includes toluene, ethyl benzene, and the like, dialkylbenzene includes xylene, diethylbenzene, and the like, and trialkylbenzene includes mesitylene and the like. An example of alkylnaphthalene includes methylnaphthalene. The above-stated aromatic ring of the aromatic hydrocarbon compound or the N-containing heterocyclic aromatic compound may have one through three substituents. In the following explanation, an aromatic hydrocarbon compound and an N-containing heterocyclic aromatic compound used in the present invention are often referred to as "aromatic compounds". Preferably, the aromatic compound is a liquid at room temperature. When a mixture of a plurality of aromatic compounds among the above-described aromatic compounds is used, the aromatic compounds need to be a liquid as the mixture. With this, the aromatic compound can be supplied to the electrode unit 100 in a liquid state without performing processes such as heating, pressurizing, and the like. Thus, the simplification of the electrochemical reduction device 10 can be achieved. The concentration of the aromatic hydrocarbon compound in a liquid state is 0.1 percent or greater, preferably 0.3 percent or greater, and more preferably 0.5 percent or greater.

[0019] The aromatic compound stored in the organic material storage tank 30 is supplied to the reduction electrode 120 of the electrode unit 100 by a first liquid supply device 32. For the first liquid supply device 32, for example, various types of pumps such as a gear pump, a cylinder pump, or the like or a gravity flow device or the like can be used. Instead of the aromatic compound, an N-substitution product of the above-stated aromatic compound may be used. A circulation pathway is provided between the organic material storage tank 30 and the reduction electrode of the electrode unit 100. An aromatic compound in which at least one benzene ring is hydrogenated by the electrode unit 100 and an unreacted aromatic compound are stored in the organic material storage tank 30 via the circulation pathway. No gas is generated by a major reaction that progresses at the reduction electrode 120 of the electrode unit 100. In the case where hydrogen is evolved as a byproduct, a gas-liquid separation device may be provided in the middle of the circulation pathway.

[0020] The water storage tank 40 stores ion-exchanged water, purified water, and the like (hereinafter, simply referred to as "water"). Water stored in the water storage tank 40 is supplied to the oxygen evolving electrode 130 of the electrode unit 100 by a second liquid supply device 42. As in the case of the first liquid supply device 32, for example, various types of pumps such as a gear pump, a cylinder pump, or the like or a gravity flow device or the like can be used for the second liquid supply device 42. A circulation pathway is provided between the water storage tank 40 and the oxygen evolving electrode of the electrode unit 100. Water that is unreacted in the electrode unit 100 is stored in the water storage tank 40 via the circulation pathway. The gas-liquid separator 50 is provided in the middle of a pathway where unreacted water is sent back to the water storage tank 40 from the electrode unit 100. The gas-liquid separator 50 separates oxygen evolved by the electrolysis of water in the electrode unit 100 from water and discharges the oxygen outside the system.

[0021] As shown in Fig. 2, the electrode unit 100 has an electrolyte membrane 110, a reduction electrode 120, an oxygen evolving electrode 130, liquid diffusion layers 140a and 140b, and separators 150a and 150b. In Fig. 1, the electrode unit 100 is simplified for illustration, and the liquid diffusion layers 140a and 140b and the separators 150a and 150 are omitted.

[0022] The electrolyte membrane 110 is formed of a material (ionomer) having protonic conductivity. While selectively conducting protons, the electrolyte membrane 110 is required to prevent substances from getting mixed or being diffused between the reduction electrode 120 and the oxygen evolving electrode 130. The thickness of the electrolyte membrane 110 is preferably from 5 to 300 μm, more preferably from 10 to 150 μm, and most preferably from 20 to 100 μm. If the thickness of the electrolyte membrane 110 is less than 5 μm, the barrier property of the electrolyte membrane 110 is lowered, and the amount of cross-leaking substances is more likely to increase. If the thickness of the electrolyte membrane 110 is more than 300 μm, ion transfer resistance becomes too large. Thus, the thickness of more than 300 μm is not preferred.

[0023] The area specific resistance, i.e., ion transfer resistance per geometric area, of the electrolyte membrane 110 is preferably 2000 $m\Omega\cdot cm^2$ or less, more preferably 1000 $m\Omega\cdot cm^2$ or less, and most preferably 500 $m\Omega\cdot cm^2$ or less. If the area specific resistance of the electrolyte membrane 110 is 2000 $m\Omega\cdot cm^2$ or greater, protonic conductivity becomes insufficient. An example of a material having protonic conductivity (which is a cation-exchanging ionomer) includes a perfluorosulfonic acid polymer such as Nafion (registered trademark), Flemion (registered trademark), etc. The ion exchange capacity (IEC) of the cation-exchanging ionomer is preferably from 0.7 to 2 meq/g and more preferably from 1 to 1.2 meq/g. If the ion exchange capacity of the cation-exchanging ionomer is less than 0.7 meq/g, ionic conductivity becomes insufficient. On the other hand, if the ion exchange capacity of the cation-exchanging ionomer is greater than 2 meq/g, the solubility of the ionomer in water becomes increased, and the strength of the electrolyte membrane 110 thus becomes insufficient.

[0024] On the electrolyte membrane 110, a reference electrode 112 is provided in an area spaced apart from the reduction electrode 120 and the oxygen evolving electrode 130 in such a manner that the reference electrode 112 is in contact with the electrolyte membrane 110. In other words, the reference electrode 112 is electrically isolated from the reduction electrode 120 and the oxygen evolving electrode 130. The reference electrode 112 is held at a reference electrode potential V_{Ref}. Examples of the reference electrode 112 include a standard hydrogen reduction electrode (reference electrode potential V_{Ref} = 0 V) and an Ag/AgCl electrode (reference electrode potential V_{Ref} = 0.199 V). However, the reference electrode 112 is not limited to these. The reference electrode 112 is preferably provided on the surface of the electrolyte membrane 110 on the side of the reduction electrode 120.

[0025] A potential difference ΔV_{CA} between the reference electrode 112 and the reduction electrode 120 is detected by a voltage detection unit 114. The value of the potential difference ΔV_{CA} detected by the voltage detection unit 114 is input to the control unit 60.

[0026] The reduction electrode 120 is provided on one side of the electrolyte membrane 110. The reduction electrode 120 is a reduction electrode catalyst layer containing a reduction catalyst for hydrogenating at least one benzene ring of an aromatic compound. A reduction catalyst used for the reduction electrode 120 is not particularly limited but is composed of, for example, a composition containing a first catalyst metal (noble metal) that contains at least one of Pt and Pd and containing one or more kinds of second catalyst metals selected from among Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ru, Sn, W, Re, Pb, and Bi. The form of the composition is an alloy of the first catalyst metal and the second catalyst metal or an intermetallic compound composed of the first catalyst metal and the second catalyst metal. The ratio of the first catalyst metal to the total mass of the first catalyst metal and the second catalyst metal is preferably from 10 to 95 wt%, and more preferably from 20 to 90 wt%, and most preferably from 25 to 80 wt%. The ratio of the first catalyst metal of less than 10 wt% may result in deterioration in durability from the perspective of resistance to dissolving or the like. On the other hand, if the ratio of the first catalyst metal is greater than 95 wt%, the properties of the reduction catalyst become similar to the properties of a noble metal alone, and the electrode activity thus becomes insufficient. In the following explanation, a first catalyst metal and a second catalyst metal are often collectively referred to as "catalyst metals".

[0027] The above-described catalyst metals may be supported by a conductive material (support). The electrical conductivity of the conductive material is preferably 1.0×10^{-2} S/cm or greater, more preferably 3.0×10^{-2} S/cm or greater, and most preferably 1.0×10^{-1} S/cm or greater. If the electrical conductivity of the conductive material is less than 1.0×10^{-2} S/cm, sufficient conductivity cannot be provided. Examples of the conductive material include a conductive material containing any one of a porous carbon, a porous metal, and a porous metal oxide as a major component. An example of the porous carbon includes carbon black such as Ketjenblack (registered trademark), acetylene black, Vulcan (registered trademark), or the like. The BET specific surface area of the porous carbon measured by a nitrogen adsorption method is preferably 100 m^2/g or greater, more preferably 150 m^2/g or greater, and most preferably 200 m^2/g or greater. If the BET specific surface area of the porous carbon is less than 100 m^2/g, it is difficult to uniformly support the catalyst metals. Therefore, the rate of utilization of a catalyst metal surface is lowered, causing the catalyst performance to be lowered. Examples of the porous metal include, for example, Pt black, Pd black, a Pt metal deposited in a fractal shape, and the like. Examples of a porous metal oxide include an oxide of Ti, an oxide of Zr, an oxide of Nb, an oxide of Mo, an oxide of Hf, an oxide of Ta, and an oxide of W. Furthermore, examples of a porous conductive material for supporting a catalyst metal include a nitride, a carbide, an oxynitride, a carbonitride, a partially-oxidized carbonitride of a metal such as Ti, Zr, Nb, Mo, Hf, Ta, W, or the like (hereinafter, these are collectively referred to as porous metal carbonitrides and the like). The respective BET specific surface areas of the porous metal, the porous metal oxide, the porous metal carbonitrides, and the like measured by a nitrogen adsorption method are preferably 1 m^2/g or greater, more preferably 3 m^2/g or greater, and most preferably 10 m^2/g or greater. If the respective BET specific surface areas of the porous metal, the porous metal oxide, the porous metal carbonitrides, and the like are less than 1 m^2/g, it is difficult to uniformly support the catalyst metals. Therefore, the rate of utilization of a catalyst metal surface is lowered, causing the catalyst performance to be lowered.

[0028] Depending on the type and composition of the first catalyst metal and the second catalyst metal, a simultaneous impregnation method or a sequential impregnation method can be employed as a method for supporting the catalyst metals on the support. The first catalyst metal and the second catalyst metal are simultaneously impregnated into the support in the simultaneous impregnation method, and the second catalyst metal is impregnated into the support after the first catalyst metal is impregnated into the support in the sequential impregnation method. In the case of the sequential impregnation method, after the first catalyst metal is loaded onto the support, a heat treatment or the like may be performed once, and the second catalyst metal may be then loaded onto the support. After the impregnation of both the first catalyst metal and the second catalyst metal is completed, the alloying of the first catalyst metal and the second catalyst metal or the formation of an intermetallic compound composed of the first catalyst metal and the second catalyst metal is performed by a heat treatment process.

[0029] A material having conductivity such as the previously-stated conductive oxide, carbon black, or the like may be added to the reduction electrode 120 in addition to a conductive compound on which a catalyst metal is supported. With this, the number of electron-conducting paths among reduction catalyst particles can be increased. Thus, resistance per geometric area of a reduction catalyst layer can be lowered in some cases.

[0030] As an additive agent, a fluorine-based resin such as polytetrafluoroethylene (PTFE) may be contained in the reduction electrode 120.

[0031] The reduction electrode 120 may contain an ionomer having protonic conductivity. Preferably, the reduction electrode 120 contains ionically conducting materials (ionomers) having a structure that is identical or similar to that of the above-stated electrolyte membrane 110 in a predetermined mass ratio. This allows the ionic conductivity of the reduction electrode 120 to be improved. In particular, in the case where a catalyst support is porous, the reduction electrode 120 makes a significant contribution to the improvement of the ionic conductivity by containing an ionomer that has protonic conductivity. An example of an ionomer having protonic conductivity (a cation-exchanging ionomer) includes a perfluorosulfonic acid polymer such as Nafion (registered trademark), Flemion (registered trademark), etc. The ion exchange capacity (IEC) of the cation-exchanging ionomer is preferably from 0.7 to 3 meq/g, more preferably from 1 to 2.5 meq/g, and most preferably from 1.2 to 2 meq/g. When a catalyst metal is supported on porous carbon (carbon support), a mass ratio I/C of the cation-exchanging ionomer (I) to the carbon support (C) is preferably from 0.1 to 2, more preferably from 0.2 to 1.5, and most preferably from 0.3 to 1.1. It is difficult to obtain sufficient ionic conductivity if the mass ratio I/C is less than 0.1. On the other hand, if the mass ratio I/C is 2 or greater, an increase in the thickness of an ionomer coating for the catalyst metal inhibits an aromatic compound, which is a reactant, from touching a catalytic site, or a decrease in the electron conductivity lowers the electrode activity.

[0032] Preferably, the ionomers contained in the reduction electrode 120 partially coat a reduction catalyst. This allows three elements (an aromatic compound, a proton, and an electron) that are necessary for an electrochemical reaction at the reduction electrode 120 to be efficiently supplied to a reaction field.

[0033] The liquid diffusion layer 140a is laminated on the surface of the reduction electrode 120 on the opposite side of the electrolyte membrane 110. The liquid diffusion layer 140a plays a function of uniformly diffusing, to the reduction electrode 120, a liquid aromatic compound supplied from the separator 150a that is described later. As the liquid diffusion layer 140a, for example, carbon paper and carbon cloth are used.

[0034] The separator 150a is laminated on the surface of the liquid diffusion layer 140a on the side opposite to the electrolyte membrane 110. The separator 150a is formed of a carbon resin, an anticorrosion alloy of Cr-Ni-Fe, Cr-Ni-Mo-Fe, Cr-Mo-Nb-Ni, Cr-Mo-Fe-W-Ni, or the like. A single or a plurality of groove-like flow channels 152a is/are provided on the surface of the separator 150a on the side of the liquid diffusion layer 140a. The liquid aromatic compound supplied from the organic material storage tank 30 circulates through the flow channel 152a. The liquid aromatic compound soaks into the liquid diffusion layer 140a from the flow channel 152a. The form of the flow channel 152a is not particularly limited. For example, a straight flow channel or a serpentine flow channel can be used. When a metal material is used for the separator 150a, the separator 150a may be a structure in which ball-like or pellet-like metal fine powder is sintered.

[0035] The oxygen evolving electrode 130 is provided on the other side of the electrolyte membrane 110. The oxygen evolving electrode 130 that contains catalysts of noble metal oxides such as RuO_2, IrO_2, and the like is preferably used. These catalysts may be supported in a dispersed manner or coated by a metal substrate such as a metal wire or mesh of metals such as Cr, Mn, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ta, W, and the like or of alloys composed primarily of these metals. In particular, since IrO_2 is high-priced, manufacturing costs can be lowered by performing thin film coating on a metal substrate when IrO_2 is used as a catalyst.

[0036] The liquid diffusion layer 140b is laminated on the surface of the oxygen evolving electrode 130 on the side opposite to the electrolyte membrane 110. The liquid diffusion layer 140b plays a function of uniformly diffusing, to the oxygen evolving electrode 130, water supplied from the separator 150b that is described later. As the liquid diffusion layer 140b, for example, carbon paper and carbon cloth are used.

[0037] The separator 150b is laminated on the surface of the liquid diffusion layer 140b on the side opposite to the electrolyte membrane 110. The separator 150b is formed of an anticorrosion alloy of Cr-Ni-Fe, Cr-Ni-Mo-Fe, Cr-Mo-Nb-Ni, Cr-Mo-Fe-W-Ni, or the like or of a material in which the surfaces of these metals are coated by an oxide layer. A single or a plurality of groove-like flow channels 152b is/are provided on the surface of the separator 150b on the side of the liquid diffusion layer 140b. The water supplied from the water storage tank 40 circulates through the flow channel 152b. The water soaks into the liquid diffusion layer 140b from the flow channel 152b. The form of the flow channel 152b is not particularly limited. For example, a straight flow channel or a serpentine flow channel can be used. When a metal material is used for the separator 150b, the separator 150b may be a structure in which ball-like or pellet-like metal fine powder is sintered.

[0038] In the present embodiment, liquid water is supplied to the oxygen evolving electrode 130. Alternatively, a humidified gas (e.g., air) may be used in place of liquid water. In this case, the dew-point temperature of the humidified gas is preferably from room temperature to 100°C and more preferably from 50 to 100°C.

[0039] When toluene is used as the aromatic compound, reactions that occur in the electrode unit 100 are as follows:

<Electrode Reaction at Oxygen Evolving Electrode>

$$3H_2O \cdot 1.5O_2 + 6H^+ + 6e^- : E_0 = 1.23\ \mathrm{V}$$

<Electrode Reaction at Reduction Electrode>

$$\text{toluene} + 6H^+ + 6e^- \rightarrow \text{methylcyclohexane} : E_0 = 0.153\ \mathrm{V}$$

(vs RHE)

[0040] In other words, the electrode reaction at the oxygen evolving electrode and the electrode reaction at the reduction electrode progress in parallel, and protons evolved by electrolysis of water are supplied to the reduction electrode via the electrolyte membrane 110 by the electrode reaction at the oxygen evolving electrode and used for hydrogenation of at least one benzene ring of the aromatic compound in the electrode reaction at the reduction electrode.

[0041] Referring back to Fig. 1, the control unit 60 controls the power control unit 20 such that a relationship, $V_{HER} - 20\ \mathrm{mV} \leq V_{CA} \leq V_{TRR}$, can be satisfied when the potential at a reversible hydrogen electrode, the standard redox potential of the aromatic compound, and the potential of the reduction electrode 120 are expressed as V_{HER}, V_{TRR}, and V_{CA}, respectively. If the potential V_{CA} is below V_{HER} - 20 mV, competition with a hydrogen generation reaction will occur, and the reduction selectivity of the aromatic compound will become insufficient. Thus, the potential V_{CA} of below V_{HER} - 20 mV is not preferred. On the other hand, the potential V_{CA} of higher than the standard redox potential V_{TRR} is not preferred since the hydrogenation of at least one benzene ring of the aromatic compound will not progress at a practically sufficient reaction speed. In other words, by setting the potential V_{CA} to be in a range that satisfies the above-stated relational expression, an electrochemical reaction can be progressed at the both electrodes, and the hydrogenation of at least one benzene ring of the aromatic compound can thus be industrially practiced.

[0042] Furthermore, the following reaction conditions are used favorably for the hydrogenation of at least one benzene ring of an aromatic compound using the electrochemical reduction device 10. The temperature of the electrode unit 100 is preferably from room temperature to 100°C and more preferably from 40 to 80°C. The temperature of the electrode unit 100 of below the room temperature is not preferred since there is a possibility that the progress of an electrolytic reaction is slowed down or an enormous amount of energy is required to remove heat generated as the reaction progresses. On the other hand, the temperature of the electrode unit 100 of above 100°C is not preferred for the electrochemical reduction device 10 in which reactions of the both electrodes are performed in a liquid phase since water will be boiled at the oxygen evolving electrode 130 and the vapor pressure of an organic substance will be increased at the reduction electrode 120. Since the reduction electrode potential V_{CA} is a true electrode potential, the reduction electrode potential VA may be different from a potential V_{CA_actual} that is actually measured. If there are resistance components, among various resistance components that exist in an electrolytic cell used in the present invention, that result in ohmic resistance, a resistance value per electrode area of the entirety of these components is set to be the entire ohmic resistance R_{ohmic}, and the true electrode potential V_{CA} is calculated using the following expression.

$$V_{CA} = V_{CA\_actual} + R_{ohmic} \times J \text{ (current density)}$$

[0043] Examples of the resistance components that result in ohmic resistance are proton transfer resistance of the electrolyte membrane, electron transfer resistance of the electrode catalyst layer, and, furthermore, contact resistance on an electric circuit. R_{ohmic} can be obtained as an actual resistance component on an equivalent circuit by using an alternating-current impedance method or an alternating-current resistance measurement at a fixed frequency. Alternatively, once the configuration of an electrolytic tank and a material system to be used are determined, a method is preferably employed where R_{ohmic} is used in the following control while considering R_{ohmic} as an almost stationary value.

[0044] Fig. 3 is a flowchart illustrating an example of potential control of the reduction electrode 120 by the control unit 60. An explanation is given in the following regarding the mode of the potential control of the reduction electrode 120 by using, as an example, a case where an Ag/AgCl electrode (reference electrode potential V_{Ref} = 0.199 V) is used.

[0045] First, a potential V_{CA} (target value) that satisfies the expression, $V_{HER} - 20 \text{ mV} \le V_{CA} \le V_{TRR}$, is set (S10). In one embodiment, the potential V_{CA} (target value) is a value that is stored in advance in memory such as ROM. In another embodiment, the potential V_{CA} (target value) is set by a user.

[0046] The potential difference ΔV_{CA} between the reference electrode 112 and the reduction electrode 120 is then detected by the voltage detection unit 114 (S20).

[0047] The control unit 60 then calculates a potential V_{CA} (actual measurement value) of the reduction electrode 120 by using an expression, $V_{CA} = OV_{CA} - V_{Ref} = \Delta V_{CA} - 0.199 \text{ V}$ (S30).

[0048] Then, the control unit 60 determined whether the potential V_{CA} (actual measurement value) satisfies the following expressions (1) and (2) (S40).

$$|\text{potential } V_{CA} \text{ (actual measurement value)} - \text{potential } V_{CA} \text{ (target value)}| \le \text{acceptable value} \quad (1)$$

$$V_{HER} - 20 \text{ mV} \le V_{CA} \text{ (actual measurement value)} \le V_{TRR} \quad (2)$$

[0049] In the above expression, the acceptable value is, for example, 1 mV.

[0050] If the potential V_{CA} (actual measurement value) satisfies the expressions (1) and (2), the step proceeds to "yes" in S40, and the process performed at this point is ended. On the other hand, if the potential V_{CA} (actual measurement value) does not satisfy the expressions (1) and (2), the step proceeds to "no" in S40, and the control unit 60 adjusts a voltage Va that is applied between the reduction electrode 120 and the oxygen evolving electrode 130 (S50). After the adjustment of the voltage Va, the process goes back to the above-stated process in S10.

[0051] An explanation is now given regarding an example for the adjustment of the voltage Va. For example, when potential V_{CA} (actual measurement value) - potential V_{CA} (target value) > acceptable value, the control unit 60 transmits to the power control unit 20 an instruction to increase the voltage Va by only 1 mV. Even when the expression, |potential V_{CA} (actual measurement value) - potential V_{CA} (target value) | ≤ acceptable value, is satisfied as a result of increasing the voltage Va, if V_{CA} (actual measurement value) is less than ($V_{HER} - V_{allow}$), the expression (2) is not satisfied. Thus, the control unit 60 instructs to lower the voltage Va by 1 mV in the following process.

[0052] On the other hand, when potential V_{CA} (actual measurement value) - potential V_{CA} (target value) < acceptable value, the control unit 60 transmits to the power control unit 20 an instruction to lower the voltage Va by only 1 mV. Even when the expression, |potential V_{CA} (actual measurement value) - potential V_{CA} (target value)| ≤ acceptable value, is satisfied as a result of lowering the voltage Va, if V_{CA} (actual measurement value) is greater than V_{TRR}, the expression (2) is not satisfied. Thus, the control unit 60 instructs to increase the voltage Va by 1 mV in the following process. In this way, the control unit 60 adjusts the voltage Va until the expressions (1) and (2) are finally satisfied.

[0053] A value (adjustment range) for increasing or decreasing the voltage Va is not limited to 1 mV. For example, the adjustment range of the voltage Va may be set to be equal to the above-stated acceptable value in a first adjustment of the voltage Va, and the adjustment range of the voltage Va may be set to be, e.g., one-fourth of the above-stated acceptable value in a second or subsequent adjustment of the voltage Va. With this, the control unit 60 can more promptly adjust the potential V_{CA} (actual measurement value) to be in a range where the expressions (1) and (2) are satisfied.

[0054] When an oxygen evolution equilibrium potential in the electrolysis of water is expressed as V_{OER}, the control unit 60 controls the power control unit 20 in such a manner that an expression, $Va \geq (V_{OER} - V_{CA})$, is satisfied. This allows a potential V_{AN} of the oxygen evolving electrode 130 to be maintained to be the oxygen evolution equilibrium potential V_{OER} or greater.

(Relationship between Toluene Reduction Property and Reduction Electrode Potential)

[0055] Using an electrode cell having composition shown in Table 1, a hydrogenation reaction of a benzene ring of toluene was performed at different reduction electrode potentials. Fig. 4 is a graph illustrating a relationship between the potential of the reduction electrode and various current density. The mass of reduction catalyst metals is 0.5 mg/cm^2.

[TABLE 1]

REDUCTION ELECTRODE				ELECTROLYTE MEMBRANE		OXYGEN EVOLVING ELECTRODE
REDUCTION CATALYST	CONDUCTIVE MATERIAL	IONOMER	DEPTH (μm)	ION CONDUCTOR	DEPTH (μm)	METAL CATALYST
Pt(50wt%), Ru(50wt%)	Ketjen black EC600JD	Nafion DE2020(EW=1100), I/C=0.8	30	Nafion NRE212CS(EW= 1100)	50	IrO_2/MO

[0056] A current density A, a current density B, and a current density C that are shown in Fig. 4 are as shown in the following.

Current density A: the entire current density flowing through the electrode cell
Current density B: current density used for the reduction of toluene that is back-calculated from the evolution amount of methylcyclohexane determined quantitatively by gas chromatography or the like
Current density C: Current density A - Current density B (current density that was not used for the reduction of toluene but was mainly used for hydrogen generation)

Faraday efficiency shown in Fig. 4 is calculated by current density B / current density A × 100 (%).
[0057] As shown in Fig. 4, if the potential of the reduction electrode is below (potential V_{HER} - 20 mV), in other words, - 20 mV, the amount of hydrogen generation is increased, and the faraday efficiency becomes below 50%. Thus, it has been verified that the potential of the reduction electrode of below - 20 mV is not preferred.

(Second Embodiment)

[0058] Fig. 5 is a schematic diagram illustrating the configuration of an electrochemical reduction device according to a second embodiment. As shown in Fig. 5, an electrochemical reduction device 10 comprises an electrode unit assembly 200, a power control unit 20, an organic material storage tank 30, a water storage tank 40, a gas-liquid separator 50, and a control unit 60. The electrode unit assembly 200 has a laminated structure where a plurality of electrode units 100 are connected in series. In the present embodiment, the number N of the electrode units 100 is five. The configuration of each electrode unit 100 is similar to the configuration according to the first embodiment. In Fig. 5, the electrode units 100 are simplified for illustration, and liquid diffusion layers 140a and 140b and separators 150a and 150 are omitted.
[0059] The positive electrode output terminal of the power control unit 20 is connected to the positive electrode terminal of the electrode unit assembly 200. On the other hand, the negative electrode output terminal of the power control unit 20 is connected to the negative electrode terminal of the electrode unit assembly 200. With this, a predetermined voltage VA is applied between the positive electrode terminal and the negative electrode terminal of the electrode unit assembly 200. A reference electrode input terminal of the power control unit 20 is connected to a reference electrode 112 provided on an electrolyte membrane 110 of a specific electrode unit 100, which will be described later, and the potential of the positive electrode output terminal and the potential of the negative electrode output terminal are determined based on the potential of the reference electrode 112.
[0060] A first circulation pathway is provided between the organic material storage tank 30 and reduction electrodes 120 of the respective electrode units 100. Aromatic compounds stored in the organic material storage tank 30 is supplied to the reduction electrodes 120 of the respective electrode units 100 by a first liquid supply device 32. More specifically, a pipeline that forms the first circulation pathway is branched on the downstream side of the first liquid supply device 32, and the aromatic compounds are supplied to the reduction electrodes 120 of the respective electrode units 100 in a distributed manner. Aromatic compounds in which at least one benzene ring are hydrogenated by the electrode units 100 and unreacted aromatic compounds merge into a pipeline that communicates with the organic material storage tank 30 and are then stored in the organic material storage tank 30 via the pipeline.
[0061] A second circulation pathway is provided between the water storage tank 40 and oxygen evolving electrodes 130 of the respective electrode units 100. Water stored in the water storage tank 40 is supplied to the oxygen evolving electrodes 130 of the respective electrode units 100 by a second liquid supply device 42. More specifically, a pipeline that forms the second circulation pathway is branched on the downstream side of the second liquid supply device 42, and the water is supplied to the oxygen evolving electrodes 130 of the respective electrode units 100 in a distributed manner. Unreacted water merges into a pipeline that communicates with the water storage tank 40 and is then stored in the water storage tank 30 via the pipeline.
[0062] On an electrolyte membrane 110 of a specific electrode unit 100, a reference electrode 112 is provided in an area spaced apart from the reduction electrode 120 and the oxygen evolving electrode 130 in such a manner that the reference electrode 112 is in contact with the electrolyte membrane 110 in the same way as in the first embodiment. The specific electrode unit 100 needs to be any one of the plurality of electrode units 100.
[0063] A potential difference ΔV_{CA} between the reference electrode 112 and the reduction electrodes 120 is detected by a voltage detection unit 114. The value of the potential difference ΔV_{CA} detected by the voltage detection unit 114 is input to the control unit 60.
[0064] The control unit 60 controls the power control unit 20 such that a relationship, $V_{HER} - 20\ \text{mV} \leq V_{CA} \leq V_{TRR}$, can be satisfied when the potential at a reversible hydrogen electrode, the standard redox potential of an aromatic compound, and the potential of the reduction electrodes 120 of the respective electrode units 100 are expressed as V_{HER}, V_{TRR}, and V_{CA}, respectively.
[0065] The mode of the potential control of the reduction electrode 120 by the control unit 60 is similar to the mode

according to the first embodiment. Note that while an applied voltage Va is adjusted by the control unit 60 in the first embodiment, a voltage VA applied between the positive electrode terminal and the negative electrode terminal of the electrode unit assembly 200 is adjusted by the control unit 60 in the present embodiment.

[0066] The control unit 60 controls the power control unit 20 in such a manner that an expression, $Va \geq (V_{OER} - V_{CA}) \times N$, is satisfied where N (two or greater) is the number of electrode units and is five in the present embodiment. This allows the potential V_{AN} to be maintained to be the oxygen evolution equilibrium potential V_{OER} or greater.

[0067] According to the present embodiment, the hydrogenation of an aromatic compound can be progressed in parallel in a plurality of electrode units. Thus, the amount of hydrogenation of at least one benzene ring of aromatic compounds per unit time can be dramatically increased. Therefore, the hydrogenation of at least one benzene ring of aromatic compounds can be industrially practiced.

(Third Embodiment)

[0068] Fig. 6 is a schematic diagram illustrating the configuration of an electrochemical reduction device according to a third embodiment. The basic configuration of an electrochemical reduction device 10 according to the present embodiment is similar to the basic configuration according to the second embodiment. In the present embodiment, an electrode unit assembly 200 is held in an electrolytic tank 300. A second circulation pathway is provided between the electrolytic tank 300 and a water storage tank 40, and the electrolytic tank 300 is filled with water supplied from the water storage tank 40. Water that fills the electrolytic tank 300 can circulate in oxygen evolving electrodes 130 of the respective electrode units 100.

[0069] In addition to effects that can be obtained in the second embodiment, the electrochemical reduction device 10 according to the present embodiment has an advantage of decreasing an in-plane temperature difference of the oxygen evolving electrodes 130, a temperature difference among electrode units, and an interelectrode temperature difference from reduction electrodes 120 by increasing the heat capacity of a water tank in the electrolytic tank.

[0070] The invention is not limited to the above-mentioned embodiments, and various modifications, such as a design change, may be added thereto on the basis of knowledge of those skilled in the art. It should be understood that any embodiment to which one or more of the modifications are added is also included in the scope of the invention. For example, in the above-described embodiments, a configuration is employed where an aromatic compound and water circulate inside a circulation pathway, and a reservoir connected to the inlet side of an electrolysis unit and a reservoir connected to the outlet side of the electrolysis unit may be provided separately.

[0071] In the above-stated embodiments, a reduction electrode 120 contains an ionomer having protonic conductivity. Alternatively, a reduction electrode 120 may contain an ionomer having hydroxy ion conductivity.

[0072] In the second and third embodiments, a reference electrode 112 is provided on an electrolyte membrane 110 of a single electrode unit. Alternatively, a reference electrode 112 may be provided on respective electrolyte membranes 110 of a plurality of electrode units 100. In this case, by the voltage detection unit 114, a potential difference ΔV_{CA} between each reference electrode 112 and a corresponding reduction electrode 120 is detected, and a potential V_{CA} is calculated by using an average value of a plurality of potential differences ΔV_{CA} that are detected. With this, a voltage VA can be adjusted to be in a more appropriate range when variation in potential is caused among the electrode units 100.

[DESCRIPTION OF THE REFERENCE NUMERALS]

[0073] 10 electrochemical reduction device, 20 power supply unit, 30 organic material storage tank, 40 water storage tank, 50 gas-liquid separator, 100 electrode unit, 112 reference electrode, 114 voltage detection unit, 110 electrolyte membrane, 120 reduction electrode, 130 oxygen evolving electrode, 140a, 140b liquid diffusion layer, 150a, 150b separator, 200 electrode unit assembly, 300 electrolytic tank

[INDUSTRIAL APPLICABILITY]

[0074] The present invention can be applied to technologies for electrochemically hydrogenating an aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound.

Claims

1. An electrochemical reduction device comprising:

an electrode unit including an electrolyte membrane having ionic conductivity, a reduction electrode that is provided on one side of the electrolyte membrane and that contains a reduction catalyst for hydrogenating at

least one benzene ring of an aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound, and an oxygen evolving electrode that is provided on the other side of the electrolyte membrane;
a power control unit that applies a voltage Va between the reduction electrode and the oxygen evolving electrode; and
a control unit that controls the power control unit such that a relationship, V_{HER} - arbitrarily-defined acceptable potential $\leq V_{CA} \leq V_{TRR}$, can be satisfied when the potential at a reversible hydrogen electrode, the standard redox potential of the aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound, and the potential of the reduction electrode are expressed as V_{HER}, V_{TRR}, and V_{CA}, respectively.

2. The electrochemical reduction device according to claim 1, wherein the arbitrarily-defined acceptable potential is 20 mV.

3. The electrochemical reduction device according to claim 1 or 2, further comprising:

a reference electrode that is arranged to be in contact with the electrolyte membrane and to be electrically isolated from the reduction electrode and the oxygen evolving electrode and that is held at a reference electrode potential V_{Ref}; and
a voltage detection unit that detects a potential difference ΔV_{CA} between the reference electrode and the reduction electrode,
wherein the control unit acquires the potential V_{CA} of the reduction electrode based on the potential difference ΔV_{CA} and the reference electrode potential V_{Ref}.

4. The electrochemical reduction device according to claim 3, wherein the control unit controls the potential V_{CA} of the reduction electrode to be in a predetermined range by changing the voltage Va.

5. The electrochemical reduction device according to claim 4, wherein, when an oxygen evolution equilibrium potential in the electrolysis of water is expressed as V_{OER}, the control unit controls the power control unit such that an expression, $Va \geq (V_{OER} - V_{CA})$, is satisfied.

6. The electrochemical reduction device according to any one of claims 3 through 5, wherein the reference electrode is arranged on the side of the electrolyte membrane on which the reduction electrode is provided.

7. An electrochemical reduction device comprising:

an electrode unit assembly in which a plurality of electrode units are electrically connected to one another in series, the electrode units each including an electrolyte membrane having ionic conductivity, a reduction electrode that is provided on one side of the electrolyte membrane and that contains a reduction catalyst for hydrogenating at least one benzene ring of an aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound, and an oxygen evolving electrode that is provided on the other side of the electrolyte membrane;
a power control unit that applies a voltage VA between a positive electrode terminal and a negative electrode terminal of the electrode unit assembly; and
a control unit that controls the power control unit such that a relationship, V_{HER} - arbitrarily-defined acceptable potential $\leq V_{CA} \leq V_{TRR}$, can be satisfied when the potential at a reversible hydrogen electrode, the standard redox potential of the aromatic hydrocarbon compound or the N-containing heterocyclic aromatic compound, and the potential of the reduction electrode of each electrode unit are expressed as V_{HER}, V_{TRR}, and V_{CA}, respectively.

8. The electrochemical reduction device according to claim 7, wherein the arbitrarily-defined acceptable potential is 20 mV.

9. The electrochemical reduction device according to claim 7 or 8, further comprising:

a reference electrode that is arranged to be in contact with an electrolyte membrane of any one of electrolytic layers contained in the electrode unit assembly and to be electrically isolated from the reduction electrode and the oxygen evolving electrode; and
a voltage detection unit that detects a potential difference ΔV_{CA} between the reference electrode and the reduction electrode,

wherein the control unit acquires the potential V_{CA} of the reduction electrode based on the potential difference ΔV_{CA} and the reference electrode potential V_{Ref}.

10. The electrochemical reduction device according to claim 9, wherein the control unit controls the potential V_{CA} of the reduction electrode of each electrode unit to be in a predetermined range by changing the voltage VA.

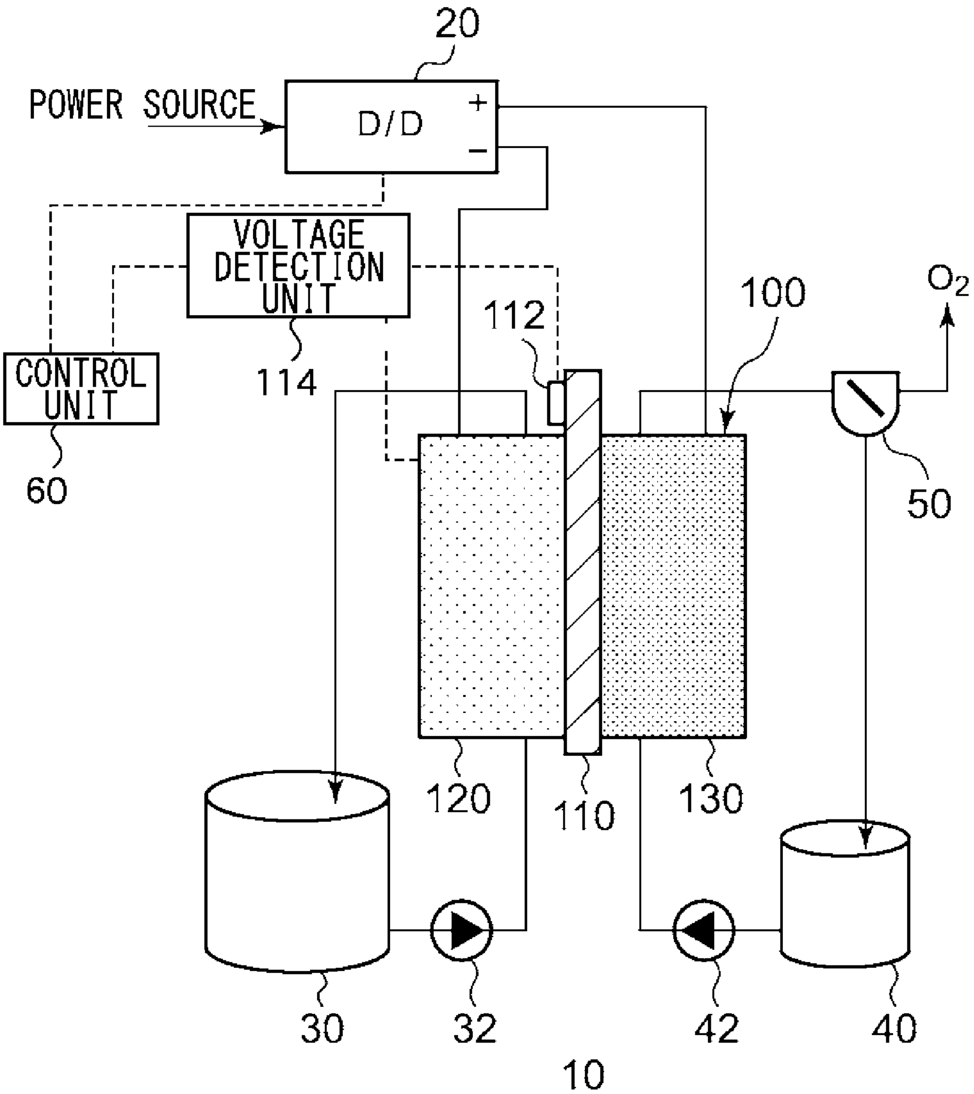
11. The electrochemical reduction device according to claim 10, wherein, when an oxygen evolution equilibrium potential in the electrolysis of water is expressed as V_{OER}, the control unit controls the power control unit such that an expression, $Va \geq (V_{OER} - V_{CA}) \times N$, is satisfied where N (two or greater) is the number of serially-concatenated electrode units.

12. The electrochemical reduction device according to any one of claims 9 through 11, wherein the reference electrode is arranged on the side of the electrolyte membrane on which the reduction electrode is provided.

13. A method for manufacturing a hydride of an aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound, comprising introducing an aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound to the reduction electrode side of the electrode unit, circulating water or a humidified gas to the oxygen evolving electrode side, and hydrogenating at least one benzene ring of the aromatic hydrocarbon compound or the N-containing heterocyclic aromatic compound introduced to the reduction electrode side, by using the electrochemical reduction device according to any one of claims 1 through 12.

14. The method for manufacturing a hydride of an aromatic hydrocarbon compound or an N-containing heterocyclic aromatic compound according to claim 13, wherein the aromatic hydrocarbon compound or the N-containing heterocyclic aromatic compound to be introduced to the reduction electrode side is introduced to the reduction electrode side in a liquid state at a reaction temperature.

FIG.1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D/D
+
−
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CONTROL UNIT
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112
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40
10

FIG.2

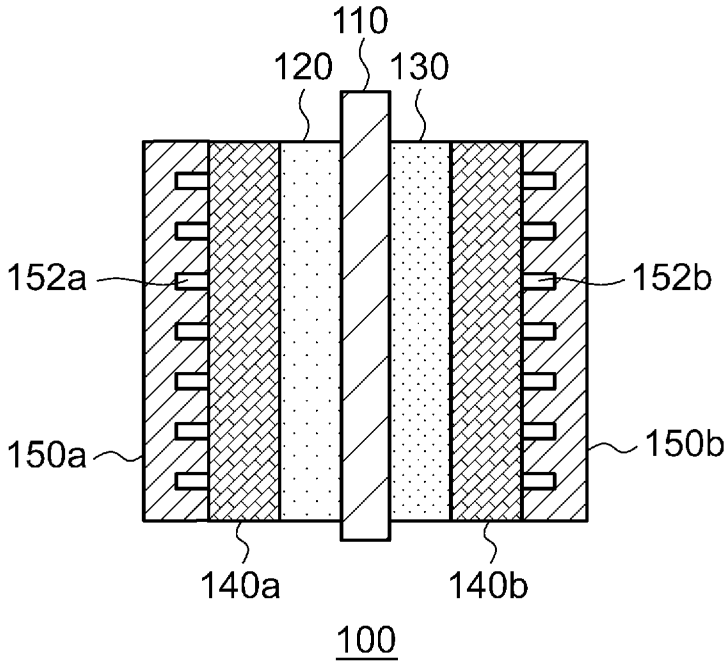


FIG.3

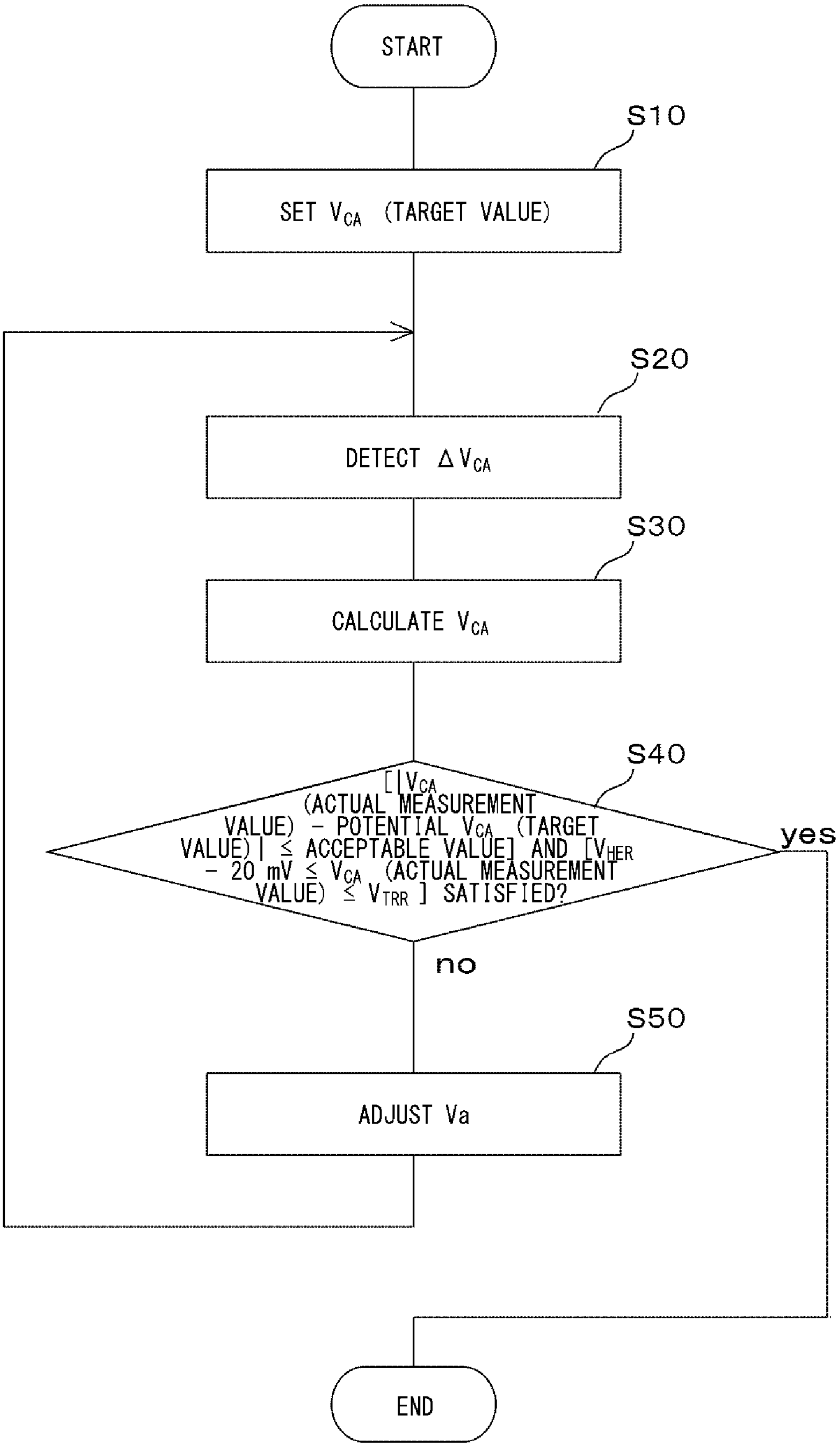
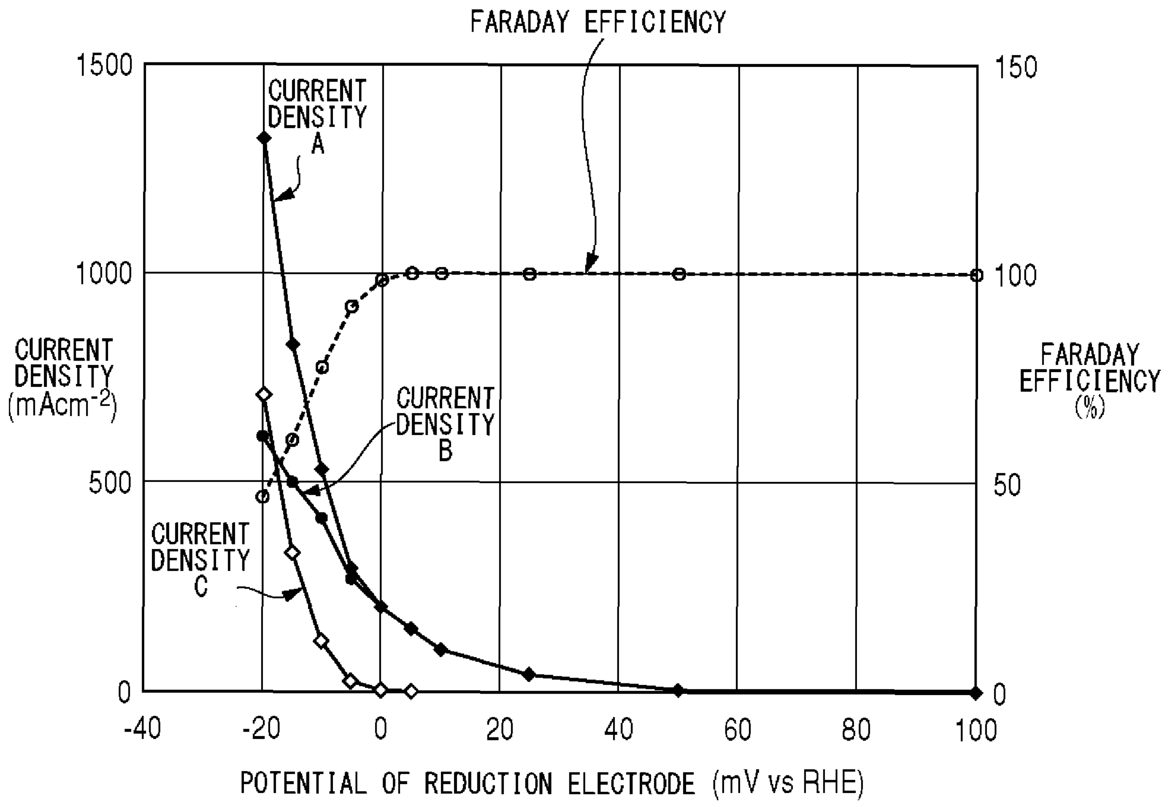

START
S10
SET V_CA (TARGET VALUE)
S20
DETECT ΔV_CA
S30
CALCULATE V_CA
S40
[|V_CA (ACTUAL MEASUREMENT VALUE) - POTENTIAL V_CA (TARGET VALUE)| ≤ ACCEPTABLE VALUE] AND [V_HER - 20 mV ≤ V_CA (ACTUAL MEASUREMENT VALUE) ≤ V_TRR] SATISFIED?
yes
no
S50
ADJUST Va
END

FIG.4


FARADAY EFFICIENCY
CURRENT DENSITY A
CURRENT DENSITY B
CURRENT DENSITY C
CURRENT DENSITY (mAcm-2)
FARADAY EFFICIENCY (%)
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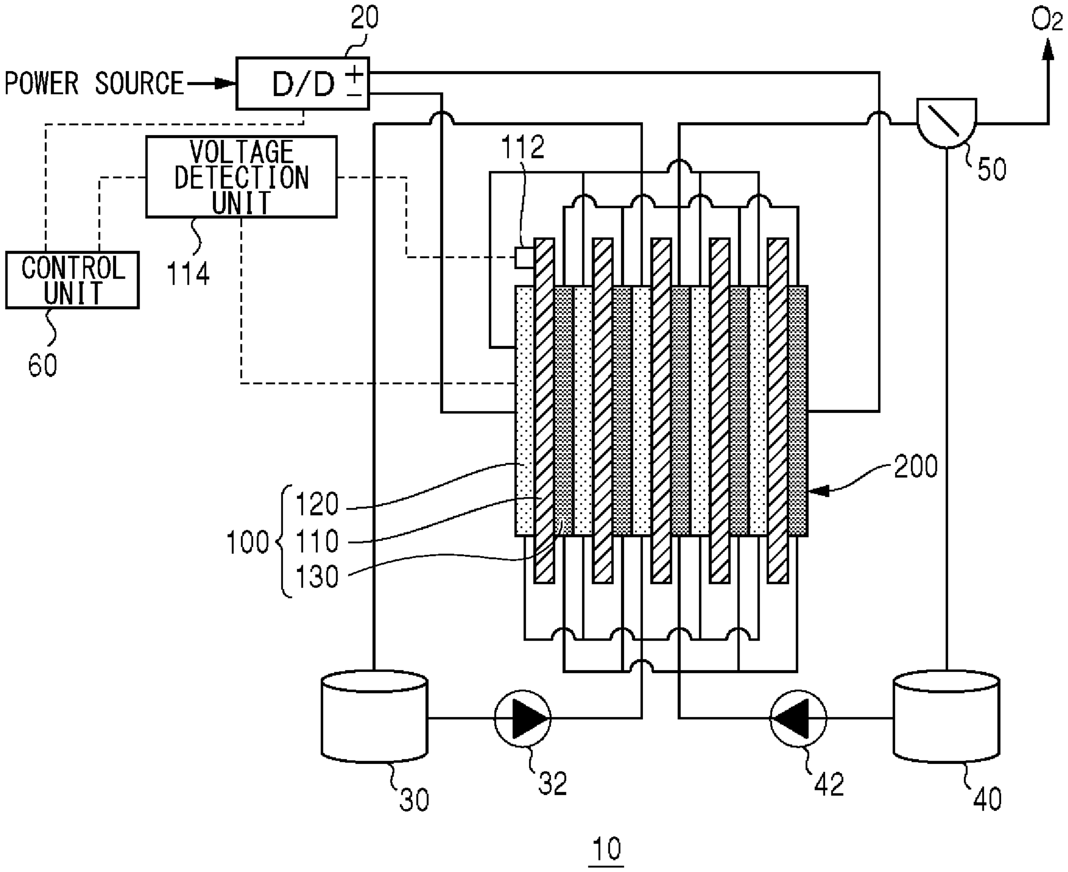
1000
500
0
150
100
50
0
-40
-20
0
20
40
60
80
100
POTENTIAL OF REDUCTION ELECTRODE (mV vs RHE)

FIG.5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CONTROL UNIT
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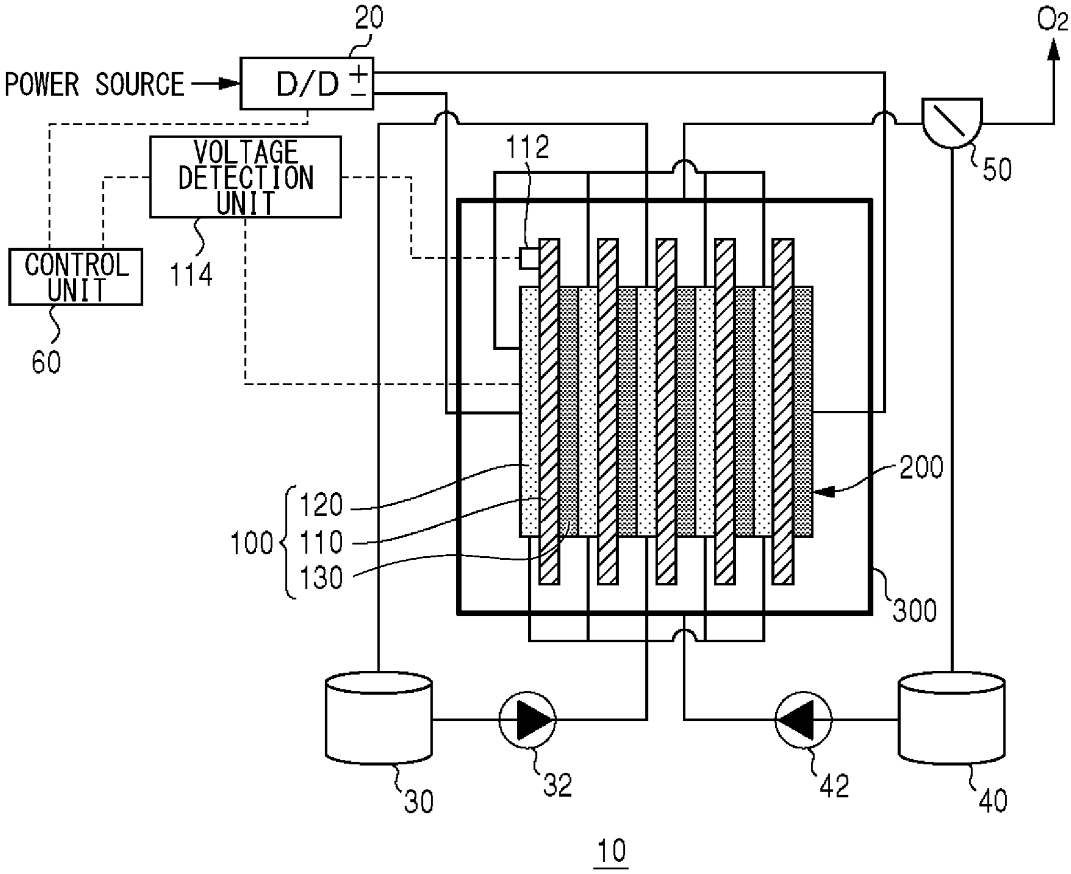
FIG.6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30
32
42
40
10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/002187

A. CLASSIFICATION OF SUBJECT MATTER
C25B15/02(2006.01)i, *C25B3/04*(2006.01)i, *C25B9/00*(2006.01)i

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)
C25B15/02, C25B3/04, C25B9/00

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2013
Kokai Jitsuyo Shinan Koho	1971-2013	Toroku Jitsuyo Shinan Koho	1994-2013

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.
Y	WO 2011/122155 A1 (Hitachi, Ltd.), 06 October 2011 (06.10.2011), claims 1 to 4; paragraphs [0017] to [0042]; fig. 1, 2 (Family: none)	1-14
Y	JP 47-27975 A (Teijin Ltd.), 30 October 1972 (30.10.1972), claims; column 5, line 17 to column 7, line 6 (Family: none)	1-14

☒ 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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"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 02 May, 2013 (02.05.13)	Date of mailing of the international search report 14 May, 2013 (14.05.13)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/002187

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 53-113828 A (BASF AG.), 04 October 1978 (04.10.1978), claim 1 & US 4145264 A & GB 1596860 A & DE 2711005 A & FR 2383999 A & CH 634090 A & DK 110878 A & IT 1095463 A & IT 1095463 B & IT 7820765 A0	1-14
Y	JP 2004-211190 A (Suga Test Instruments Co., Ltd.), 29 July 2004 (29.07.2004), paragraph [0027] & JP 3452140 B	7-14
Y	JP 2009-215647 A (Tokyo Institute of Technology), 24 September 2009 (24.09.2009), paragraph [0057] (Family: none)	7-14

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- JP 2003045449 A **[0003]**
- JP 2005126288 A **[0003]**
- JP 2005239479 A **[0003]**

Non-patent literature cited in the description

- **MASARU ICHIKAWA.** *J. Jpn. Inst. Energy,* 2006, vol. 85, 517 **[0004]**