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(54) ELECTROLYSIS DEVICE

(57) An electrolysis device in an embodiment includes an electrolysis cell including: a cathode chamber in which a reduction electrode is arranged and to which a gaseous substance to be reduced is supplied; an anode chamber in which an oxidation electrode is arranged and to which a substance to be oxidized in a liquid state or in a state of vaporized liquid is supplied; and a diaphragm provided between the cathode chamber and the anode chamber. At least one of the reduction electrode and the diaphragm includes a composite containing at least an inorganic oxide fine particle and an organic polymer material which binds the inorganic oxide fine particle.

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Description

FIELD

[0001] Embodiments disclosed herein relate to an electrolysis device.

BACKGROUND

[0002] The amount of production of ammonia is about 140 million tons in the world in a year and continues to rise. About 80% of the amount of production is utilized as a raw material for fertilizer and is mainly converted to other nitrogen compounds such as urea, nitric acid, ammonium nitrate, and ammonium sulfate. On the other hand, the remaining 20% thereof is utilized for manufacture of synthetic resin and fiber. To cope with the global population growth, the shortage of cultivated acreage, and the food shortages due to the sophistication of diet mainly in developing countries, the demand for ammonia is increased. Further, ammonia attracts attention as a use of an energy carrier owing to its ease of handling, high energy density, and a characteristic of containing no carbon and emitting no carbon dioxide when used.

[0003] At present, ammonia is industrially synthesized from a hydrogen gas and a nitrogen gas derived from fossil fuels such as petroleum, coal, or natural gas by the method called the Haber-Bosh process invented about 100 years ago. This synthesis reaction requires severe conditions such as high temperature (400 to 650°C) and high pressure (200 to 400 atm), consumes 1.2% of total energy in the world, and therefore emits a large amount of carbon dioxide. To form a sustainable society in the future, the development of an alternative process with low dependence on fossil fuels is expected.

[0004] Regarding the above point, a catalyst for producing ammonia from nitrogen at normal temperature and pressure in an electrolysis method and an electrolysis device for manufacturing ammonia (NH_3) by reducing nitrogen (NH_3) by electrolysis is under development. For example, it has been reported that a molybdenum iodide complex having a PNP (2,6-bis(di-tert-butylphosphinomethyl)pyridine) ligand as a catalyst, alcohol or water as a proton source, and a solution containing a halide (II) of a lanthanoid metal, for example, samarium (II) iodide as a reducing agent are stirred in the presence of a nitrogen gas at normal temperature to thereby produce up to 4350 equivalents of ammonia per catalyst. In addition, the method using the molybdenum iodide complex having the PNP ligand as the catalyst and using a solution used in a cathode tank or both an electrolyte membrane and the solution used in the cathode tank as the proton source has been reported.

[0005] In the above electrolysis device which manufactures ammonia (NH_3) by the reduction of nitrogen (N_2) or the like, it is a problem that the manufacturing efficiency and the recovery efficiency of an electrolysis product such as ammonia decrease depending on the configuration of components such as a reduction electrode which reduces a nitrogen gas to produce ammonia, a diaphragm (separator) arranged between the reduction electrode and an oxidation electrode, and so on. For example, for the diaphragm, an ion-exchange resin film is applied, but the ion-exchange resin film is high in permeability of liquid such as an electrolytic solution to cause a flooding phenomenon on the reduction electrode side to which gas to be reduced is supplied. The flooding phenomenon becomes a cause of decreasing the production efficiency and the recovery efficiency of the electrolysis product such as ammonia on the reduction electrode side. Hence, it is required to suppress the decrease in the manufacturing efficiency and the recovery efficiency of the electrolysis product such as ammonia due to the diaphragm or the like to increase the manufacturing efficiency and the recovery efficiency of the electrolysis product. Such an object is required not only in a nitrogen electrolysis device which manufactures ammonia by reduction of nitrogen but also in electrolysis devices such as a water electrolysis device which electrolyzes water (H_2O) to produce hydrogen (H_2) and a carbon dioxide electrolysis device which electrolyzes carbon dioxide (CO_2) to produce a carbon compound such as carbon monoxide (CO), formic acid (HCOOH), ethanol (C_2H_5OH), or the like.

SUMMARY

[0006] A problem to be solved by the present invention is to provide an electrolysis device which manufactures a reduction product such as ammonia by an electrolytic reaction with high efficiency and can increase the recovery efficiency of the reduction product.

[0007] According to the embodiments of the present invention, an electrolysis device which manufactures a reduction product by an electrolytic reaction with high efficiency and can increase the recovery efficiency of the reduction product is provided.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008]

FIG. 1 is a diagram illustrating an ammonia manufacturing apparatus in an embodiment.

FIG. 2 is a diagram illustrating a first example of an electrochemical reaction unit of the ammonia manufacturing apparatus illustrated in FIG. 1.

FIG. 3 is a diagram illustrating a second example of the electrochemical reaction unit of the ammonia manufacturing apparatus illustrated in FIG. 1.

DETAILED DESCRIPTION

[0009] An electrolysis device in an embodiment includes an electrolysis cell including: a cathode chamber in which a reduction electrode is arranged and to which a gaseous substance to be reduced is supplied; an anode chamber in which an oxidation electrode is arranged and to which a substance to be oxidized in a liquid state or in a state of vaporized liquid is supplied; and a diaphragm provided between the cathode chamber and the anode chamber. In the electrolysis device in the embodiment, at least one of the reduction electrode and the diaphragm includes a composite containing at least an inorganic oxide fine particle and an organic polymer material which binds the inorganic oxide fine particle.

[0010] Hereinafter, electrolysis devices in embodiments will be explained with reference to the drawings. In the embodiments explained below, substantially the same components are denoted by the same reference signs and the explanation thereof will be partially omitted in some cases. The drawings are schematic in which the relationship between the thickness and planar dimension, a thickness ratio among the components, and so on may be different from actual ones. As the electrolysis devices in the embodiments, a nitrogen electrolysis device which manufactures ammonia (NH_3) by the reduction of nitrogen (N_2) will be mainly explained here, but the electrolysis devices in the embodiments are not limited to the nitrogen electrolysis device. The electrolysis devices in the embodiments may be, for example, a water electrolysis device which electrolyzes water (H_2O) to produce hydrogen (H_2) and so on, a carbon dioxide electrolysis device which electrolyzes carbon dioxide (CO_2) to produce a carbon compound such as carbon monoxide (CO), formic acid (HCOOH), methanol (CH_3OH), and the like.

[0011] FIG. 1 is a diagram illustrating a nitrogen electrolysis device 1 as an electrolysis device in an embodiment. The nitrogen electrolysis device 1 illustrated in FIG. 1 is an ammonia manufacturing apparatus, and includes: an electrochemical reaction unit (electrolysis cell) 5 including a first reaction tank (reduction reaction electrolytic tank) 2 to which gaseous nitrogen is supplied, a second reaction tank (oxidation reaction electrolytic tank) 3 to which an electrolytic solution containing water or water vapor is supplied, and a diaphragm 4; a nitrogen supply unit 7 including a nitrogen supplier (supply device) 6 for supplying nitrogen to the first reaction tank 2; an ammonia collection unit 9 including a collector (collection device) 8 which collects ammonia contained gas exhausted from the first reaction tank 2; and an ammonia separation unit 11 including an ammonia separator (separation device) 10 which separates ammonia contained in the electrolytic solution discharged from the second reaction tank 3. The nitrogen electrolysis device 1 further includes an electrolytic solution circulation unit 13 including a circulation pipe 12 for circulating a second electrolytic solution accommodated in the second reaction tank 3 outside the second reaction tank 3. Hereinafter, the components will be explained in detail.

[0012] FIG. 2 illustrates a first example of the electrochemical reaction unit 5. The electrochemical reaction unit 5 illustrated in FIG. 2 includes the first reaction tank (reduction reaction electrolytic tank) 2 as a cathode chamber, the second reaction tank (oxidation reaction electrolytic tank) 3 as an anode chamber, the diaphragm 4 provided between the first reaction tank 2 and the second reaction tank 3, a reduction electrode 14 arranged in the first reaction tank 2 and used for an electrochemical reduction reaction, and an oxidation electrode 15 arranged in the second reaction tank 3 and used for an electrochemical oxidation reaction, and they constitute an electrochemical reaction cell (electrolysis cell). The electrochemical reaction cell 5 is separated into the first reaction tank 2 and the second reaction tank 3 by the diaphragm 4 which can move ions such as hydrogen ion (H^+), hydroxide ion (OH^-), and so on. Into the first reaction tank 2, gaseous nitrogen (N_2) is supplied via a pipe. Into the second reaction tank 3, an electrolytic solution containing water (H_2O) or water vapor (H_2O) is supplied via the circulation pipe 12.

[0013] The electrochemical reaction unit 5 may have a configuration as illustrated in FIG. 3. FIG. 3 illustrates a second example of the electrochemical reaction unit 5. The electrochemical reaction unit 5 illustrated in FIG. 3 includes a third reaction tank 16 which is provided between the first reaction tank 2 supplied with the gaseous nitrogen (N_2) and the diaphragm 4 and to which the electrolytic solution (cathode solution) containing water is supplied. The first reaction tank 2 and the third reaction tank 16 are in contact with each other via the reduction electrode 14 in a porous state, and they constitute the cathode chamber. The cathode chamber having the first reaction tank 2 and the third reaction tank 16 is in contact with the second reaction tank 3 as the anode chamber via the diaphragm 4 and the oxidation electrode 15 in a porous state. The electrochemical reaction unit 5 illustrated in FIG. 3 can dissolve ammonia (NH_3) produced by reducing the gaseous nitrogen (N_2) supplied to the first reaction tank 2 in the electrolytic solution (cathode solution) supplied to the third reaction tank 16 to take them to the outside of the electrochemical reaction cell (electrolysis cell) 5. This can enhance the recovery efficiency of ammonia.

[0014] The reduction electrode 14 and the oxidation electrode 15 are connected to an external electrode 17. By feeding

power to the reduction electrode 14 and the oxidation electrode 15 from the external electrode 17, a reduction reaction occurs at the reduction electrode 14 and an oxidation reaction occurs at the oxidation electrode 15. In the second reaction tank 3, for example, water (H_2O) in the electrolytic solution is oxidized at the oxidation electrode 15 to produce oxygen (O_2) and hydrogen ions (H^+) and electrons (e^-). The produced oxygen is discharged together with water from the second reaction tank 3 via the circulation pipe 12. In the first reaction tank 2, nitrogen (N_2) is reduced by an ammonia production catalyst to produce ammonia (NH_3). The nitrogen containing ammonia is led to the outside of the first reaction tank 2 via a pipe and continuously sent to the ammonia collection unit 9. Further, a part of ammonia produced in the first reaction tank 2 moves to the second reaction tank 3 through the diaphragm 4. The electrolytic solution containing water or water vapor mixed with ammonia in the second reaction tank 3 is led to the outside of the second reaction tank 3 via the circulation pipe 12 and continuously or intermittently sent to the ammonia separation unit 11.

[0015] To the second reaction tank 3, the electrolytic solution containing water (H_2O) or water vapor is supplied as explained above. The electrolytic solution may be an aqueous solution containing an electrolyte or the like. It is preferable that the electrolytic solution is high in ion conductivity and the electrolyte itself does not react. Examples of the electrolyte contained in the electrolytic solution include lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), lithium chloride (LiCl), sodium chloride (NaCl), potassium chloride (KCl), lithium bromide (LiBr), sodium bromide (NaBr), potassium bromide (KBr), lithium iodide (LiI), sodium iodide (NaI), potassium iodide (KI), lithium nitrate (LiNOs), sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3), lithium sulfate (Li_2SO_4), sodium sulfate (Na_2SO_4), potassium sulfate (K_2SO_4), lithium hydrogen sulfate ($LiHSO_4$), sodium hydrogen sulfate ($NaHSO_4$), potassium hydrogen sulfate ($KHSO_4$), lithium peroxodisulfate ($Li_2S_2O_8$), sodium peroxodisulfate ($Na_2S_2O_8$), potassium peroxodisulfate ($K_2S_2O_8$), lithium phosphate (Li_3PO_4), sodium phosphate (Na_3PO_4), potassium phosphate (K_3PO_4), dilithium hydrogen phosphate (Li_2HPO_4), disodium hydrogen phosphate (Na_2HPO_4), dipotassium hydrogen phosphate (K_2HPO_4), lithium dihydrogen phosphate (LiH_2PO_4), sodium dihydrogen phosphate (NaH_2PO_4), potassium dihydrogen phosphate (KH_2PO_4), lithium hydrogen carbonate ($LiHCO_3$), sodium hydrogen carbonate ($NaHCO_3$), potassium hydrogen carbonate ($KHCO_3$), lithium carbonate (Li_2CO_3), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), lithium tetraborate ($Li_2B_4O_7$), sodium tetraborate ($Na_2B_4O_7$), potassium tetraborate ($K_2B_4O_7$), lithium silicate (Li_2SiO_3), sodium silicate (Na_2SiO_3), potassium silicate (K_2SiO_3), ionic liquid, and so on. It is preferable to use water as the solvent. The electrolyte concentration in the electrolytic solution is preferable, for example, in a range of 0.001 to 1 mol/L.

[0016] As the positive ion of the ionic liquid, an ion such as an imidazolium ion, a pyridinium ion, a pyrrolidinium ion, or a piperidinium ion is used. Examples of the imidazolium ion include 1-ethyl-3-methylimidazolium, 1-methyl-3-propylimidazolium, 1-butyl-3-methylimidazolium, 1-methyl-3-pentylimidazolium, 1-hexyl-3-methylimidazolium, and so on. A 2nd position of the imidazolium ion may be substituted. Examples of the substituted one include 1-ethyl-2,3-dimethylimidazolium, 1,2-dimethyl-3-propylimidazolium, 1-butyl-2,3-dimethylimidazolium, 1,2-dimethyl-3-pentylimidazolium, 1-hexyl-2,3-dimethylimidazolium, and so on. Examples of the pyridinium ion include methylpyridinium, ethylpyridinium, propylpyridinium, butylpyridinium, pentylpyridinium, hexylpyridinium, and so on. Examples of the pyrrolidinium ion include ethyl-methylpyrrolidinium, methyl-propylpyrrolidinium, butyl-methylpyrrolidinium, methyl-pentylpyrrolidinium, hexyl-methylpyrrolidinium, and so on. Examples of the piperidinium ion include ethyl-methylpiperidinium, methyl-propylpiperidinium, butyl-methylpiperidinium, methyl-pentylpiperidinium, hexyl-methylpiperidinium, and so on. In all of the imidazolium ion, pyridinium ion, pyrrolidinium ion, and piperidinium ion, the alkyl group may be substituted, and an unsaturated bond may exist. As the positive ion of the ionic liquid, a single cation or a plurality of cations combined are used.

[0017] Examples of the negative ion of the ionic liquid include a fluoride ion, a chloride ion, a bromide ion, an iodide ion, an acetate ion, a nitrate ion, a hydrogen sulfate ion, a phosphate ion, a dicyanamide ion, $BF4^-$, PF_6^-, CF_3COO^-, $CF_3SO_3^-$, SCN^-, $(CF_3SO_2)_3C^-$, a bis(trifluoromethoxysulfonyl)imide ion, a bis(trifluoromethoxysulfonyl)imide ion, a bis(perfluoroethylsulfonyl)imide ion, and so on. As the negative ion of the ionic liquid, a single anion or a plurality of anions combined are used. Further, a dipolar ion made by connecting the cation and the anion of the ionic liquid by hydrocarbon may be used. One type of the ionic liquid may be used alone or two or more types may be used in combination.

[0018] The second reaction tank 3 has the oxidation electrode 15 arranged therein, and is supplied with the electrolytic solution. At the oxidation electrode 15, when the hydrogen ion concentration of the electrolytic solution is 7 or less ($pH \leq 7$), H_2O is oxidized to produce O_2 and H^+. On the other hand, when the hydrogen ion concentration of the electrolytic solution is greater than 7 ($pH > 7$), OH^- is oxidized to produce O_2 and H_2O. The oxidation electrode 15 is constituted of a material which decreases the activation energy for causing an oxidation reaction. In other words, the oxidation electrode 15 is constituted of a material which decreases the overvoltage when causing a reaction of oxidizing H_2O or OH^- to pull out electrons. Examples of the constituent material of the oxidation electrode 15 include binary metal oxides such as platinum (Pt), manganese oxide (Mn-O), iridium oxide (Ir-O), nickel oxide (Ni-O), cobalt oxide (Co-O), iron oxide (Fe-O), tin oxide (Sn-O), indium oxide (In-O), and ruthenium oxide (Ru-O), ternary metal oxides such as Ni-Co-O, La-Co-O, Ni-La-O, and Sr-Fe-O, quaternary metal oxides such as Pb-Ru-Ir-O and La-Sr-Co-O, and metal complexes such as a Ru complex and a Fe complex.

[0019] The first reaction tank 2 has the reduction electrode 14 arranged therein, and is supplied with the nitrogen gas. When carrying out the reduction reaction, the reduction electrode 14 is preferably constituted of an electrode material

having conductivity. Besides, the reduction electrode 14 preferably has a porous structure because the reaction area can be increased by gas diffusibility. Specifically, the reduction electrode 14 preferably has a gas diffusion layer and a catalyst layer. For the gas diffusion layer, for example, carbon paper, carbon cloth, carbon felt, or the like is used. The catalyst layer contains a porous carbon material as a catalyst support, an inorganic oxide fine particle, and a polymer material which binds the porous carbon material as the catalyst support and the inorganic oxide fine particle, in addition to the reduction catalyst which reduces nitrogen to produce ammonia. The inorganic oxide fine particle is an ion conductor as will be explained later, which can enhance the transmissibility and supplyability of the hydrogen ion (H^+) and hydroxide ion (OH^-) with respect to the reduction catalyst to enhance the reduction efficiency of nitrogen (N), namely, the production efficiency of ammonia (NH_3).

[0020] The reduction catalyst (ammonia production catalyst) used at the reduction electrode 14 promotes the production of ammonia from nitrogen and, for example, a molybdenum complex is used but not limited to this. Examples of the ammonia production catalyst include (A) to (D) molybdenum complexes explained below.

[0021] A first example is (A) a molybdenum complex having, as a PCP ligand, N,N-bis(dialkylphosphinomethyl) dihydrobenzimidazolidene (where two alkyl groups may be the same or different, and at least one hydrogen atom of a benzene ring may be substituted with an alkyl group, an alkoxy group, or a halogen atom).

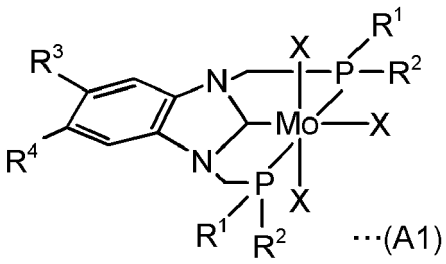
[0022] A second example is (B) a molybdenum complex having, as a PNP ligand, 2,6-bis(dialkylphosphinomethyl) pyridine (where two alkyl groups may be the same or different, and at least one hydrogen atom of a pyridine ring may be substituted with an alkyl group, an alkoxy group, or a halogen atom).

[0023] A third example is (C) a molybdenum complex having, as a PPP ligand, bis(dialkylphosphinomethyl)arylphosphine (where two alkyl groups may be the same or different).

[0024] A fourth example is (D) a molybdenum complex expressed by trans-$Mo(N_2)_2$ $(R1R2R3P)_4$ (where R1, R2, R3 are arealkyl groups or aryl groups which may be the same or different, and two R3s may connect with each other to form an alkylene chain).

[0025] In the above molybdenum complexes, the alkyl group may be, for example, a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, or the like, or may be a straight chain or branched alkyl group of a structural isomer of them, or a cyclic alkyl group such as a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, or a cyclohexyl group. The carbon number of the alkyl group is preferably 1 to 12, and more preferably 1 to 6. The alkoxy group may be, for example, a methoxy group, an ethoxy group, a propoxy group, a butoxy group, a pentoxy group, a hexyloxy group, or the like, or may be a straight chain or branched alkoxy group of a structural isomer of them, or a cyclic alkoxy group such as a cyclopropoxy group, a cyclobutoxy group, a cyclopentoxy group, or a cyclohexyloxy group. The carbon number of the alkoxy group is preferably 1 to 12, and more preferably 1 to 6. Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom, an iodine atom, and so on.

[0026] An example of the (A) molybdenum complex is a molybdenum complex expressed by Formula (A1) below.

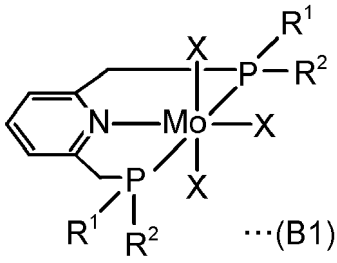


···(A1)

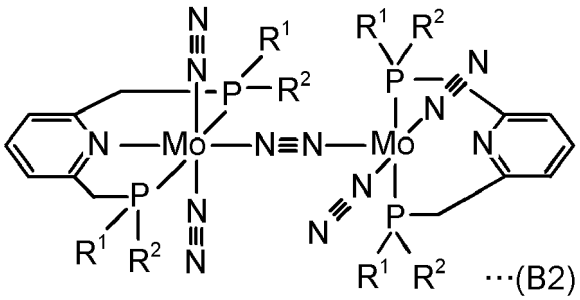
[0027] In the formula, R1 and R2 may be the same or different alkyl groups, X is an iodine atom, a bromine atom, or a chlorine atom, and at least one hydrogen atom on the benzene ring may be substituted with an alkyl group, an alkoxy group, or a halogen atom.

[0028] Examples of the alkyl group, alkoxy group, and halogen atom include those already exemplified. R1 and R2 are preferably bulky alkyl groups (for example, tert-butyl groups or isopropyl groups). It is preferable that the hydrogen atom on the benzene ring is not substituted or that hydrogen atoms at position 5 and position 6 are substituted with chain, cyclic, or branched alkyl groups with 1 to 12 carbons.

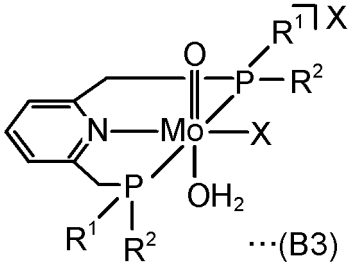
[0029] An example of the (B) molybdenum complex is a molybdenum complex expressed by Formula (B 1), Formula (B2), and Formula (B3) below.



···(B1)



···(B2)

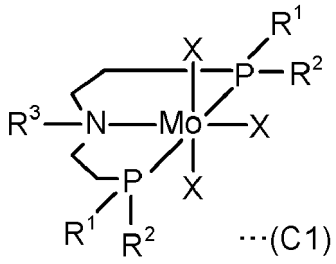


···(B3)

[0030] In the formula, R1 and R2 may be the same or different alkyl groups, X is an iodine atom, a bromine atom, or a chlorine atom, and at least one hydrogen atom on the pyridine ring may be substituted with an alkyl group, an alkoxy group, or a halogen atom.

[0031] Examples of the alkyl group, alkoxy group, and halogen atom include those already exemplified. R1 and R2 are preferably bulky alkyl groups (for example, tert-butyl groups or isopropyl groups). It is preferable that the hydrogen atom on the pyridine ring is not substituted or that a hydrogen atom at position 4 is substituted with a chain, cyclic, or branched alkyl group with 1 to 12 carbons.

[0032] An example of the (C) molybdenum complex is a molybdenum complex expressed by Formula (C1) below.

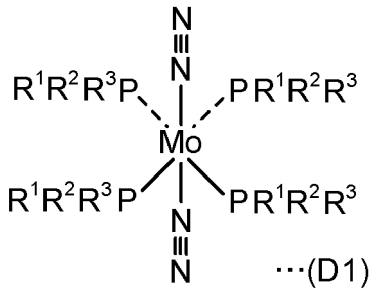


···(C1)

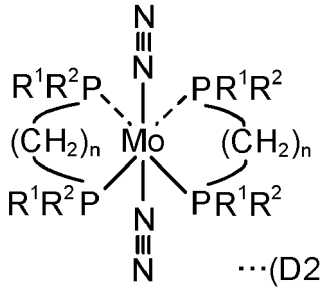
[0033] In the formula, R1 and R2 may be the same or different alkyl groups, R3 is an aryl group, and X is an iodine atom, a bromine atom, or a chlorine atom.

[0034] Examples of the alkyl group include those already exemplified. Examples of the aryl group include a phenyl group, a tolyl group, a xylyl group, a naphthyl group, the one in which at least one of cyclic hydrogen atoms of them is substituted with an alkyl group or a halogen atom, and so on. Examples of the alkyl group and halogen atom include those already exemplified. R1 and R2 are preferably bulky alkyl groups (for example, tert-butyl groups or isopropyl groups). R3 is preferably, for example, a phenyl group.

[0035] An example of the (D) molybdenum complex is a molybdenum complex expressed by Formula (D 1) and Formula (D2) below.



···(D1)

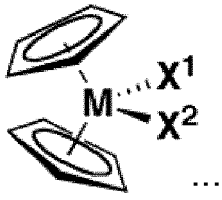


···(D2)

[0036] In the formula, R1, R2, and R3 may be the same or different alkyl groups or aryl groups, and n is 2 or 3.

[0037] Examples of the alkyl group and the aryl group include those already exemplified. In Formula (D1), it is preferable that R1 and R2 are aryl groups (for example, phenyl groups) and R3 is an alkyl group with 1 to 4 carbons (for example, a methyl group), or that R1 and R2 are alkyl groups with 1 to 4 carbons (for example, methyl groups) and R3 is an aryl group (for example, a phenyl group). In Formula (D2), it is preferable that R1 and R2 are aryl groups (for example, phenyl groups) and n is 2.

[0038] The ammonia production catalyst (reduction catalyst) which promotes the production of ammonia from nitrogen may be, for example, a metallocene complex expressed by Formula (E1) below.



···(E1)

[0039] In the formula, M is a tetravalent metal ion, and is one of titanium, zirconium, and hafnium. X1 and X2 are the same or different negative ions having a coordination property. The negative ion is preferably Cl^-, Br^-, I^-, CH_3^- or OH , and more preferably Cl^- among them. Specifically, it is desirably a metallocene complex such as bis(cyclopentadienyl)titanium dichloride or bis(cyclopentadienyl)zirconium dichloride.

[0040] Further, as the ammonia production catalyst (reduction catalyst), a metal catalyst such as molybdenum, bismuth, iron, rhodium, ruthenium, titanium, or zirconium may be used. One of them may be used alone or two or more of them may be used in combination.

[0041] The catalyst support supports the ammonia production catalyst (reduction catalyst), and a porous carbon material is used. Examples of the porous carbon material (carbon particle) include channel black, furnace black, thermal black, acetylene black, activated carbon, natural graphite, artificial graphite, graphitized carbon, graphene, carbon nanotube (CNT), fullerene, ketjen black, glassy carbon, and so on. The use of the porous carbon material as the catalyst support makes it possible to densely and efficiently fix the ammonia production catalyst to the electrode. Accordingly, it becomes possible to realize a three-phase interface control type reduction electrode 14 where nitrogen (N_2) can directly react. This can greatly enhance the production efficiency of ammonia by a gas phase.

[0042] The ammonia production catalyst is held by being adsorbed on the surface of the porous carbon particle and thereby can be used as the catalyst support for the reduction reaction of nitrogen. For example, when the ammonia production catalyst is the molybdenum complex, the porous carbon particle is brought into contact with a solution in which the molybdenum complex is dissolved to cause adsorption on the surface of the porous carbon particle. As the characteristic of the porous carbon particle capable of preferably holding the ammonia production catalyst, the specific surface area of the porous carbon particle is preferably 800 m^2/g or more and 2000 m^2/g or less for increasing the reaction

area.

[0043] The characteristic of the porous carbon material can be evaluated by a gas adsorption method by a specific surface area measurement device. For measuring the specific surface area, an inert gas (adsorbate) which reversibly adsorbs nitrogen, argon, or krypton is used. In a measurement operation, a sample is put into a sample tube with a known volume, an extraneous matter is removed from the sample by heated vacuum drying, then a fixed amount of adsorbate is introduced into the sample tube, and the adsorbate is brought into contact with the sample surface. The adsorption amount increases with time, and the increase in adsorption amount stops in due time. The state at the time is called an adsorption equilibrium state, the adsorption amount is called an equilibrium adsorption amount, and a pressure is called an equilibrium pressure. The adsorption amount is found by measuring a change in pressure until the adsorption equilibrium state is reached. For the specific surface area, an amount of an adsorption first layer is calculated from the amount of adsorbate adsorbed to the sample surface by a BET theory, and a specific surface area value is found using the area occupied by one molecule of the adsorbate.

[0044] When the ammonia production catalyst is a molecular catalyst such as a molybdenum complex, the solubility of the molecular catalyst in a solvent affects the difficulty of adsorption on the surface of the porous carbon material. Examples of the solvent to dissolve the molybdenum complex include methanol, ethanol, 1-propanol, 2-propanol, hexafluoro-2-propanol, tetrahydrofuran, acetone, acetonitrile, chloroform, and so on. Among these, methanol is preferably used because it has characteristics such as a low boiling point, high solubility, and the like. The temperature at which the molybdenum complex is adsorbed on the porous carbon material is preferably 0 to 90°C, and more preferably 5 to 40°C, taking into consideration the decomposition temperature of the molybdenum complex and the boiling point of the solvent. If the time for adsorption of the molybdenum complex on the porous carbon material is short, adsorption may not be completed. On the other hand, if the adsorption time is too long, workability will deteriorate. Therefore, the time for adsorption of the molybdenum complex on the porous carbon material is preferably in a range of 30 minutes to 48 hours, and more desirably 1 hour to 24 hours.

[0045] The inorganic oxide fine particle functions as an ion conductor in the catalyst layer and undertakes a role of supplying ions required for the reaction of the ammonia production catalyst. When the hydrogen ion concentration in the electrolytic solution is 7 or less ($pH \leq 7$), hydrogen ions (H^+) are supplied to the ammonia production catalyst, whereas when the hydrogen ion concentration in the electrolytic solution is greater than 7 ($pH > 7$), hydroxide ions (OH^-) are supplied to the ammonia production catalyst. When the catalyst layer does not contain the inorganic oxide fine particle, the catalyst layer is composed of a composite containing the porous carbon material which supports the ammonia production catalyst, the inorganic oxide fine particle, and a polymeric material which binds the porous carbon material and the inorganic oxide fine particle, and thereby can enhance the transmissibility and supplyability of hydrogen ions (H^+) and hydroxide ions (OH^-) with respect to the reduction catalyst. Accordingly, the reduction efficiency of nitrogen (N) and the initial reduction efficiency of nitrogen can be enhanced, and therefore the production efficiency of ammonia (NH_3) can be improved.

[0046] As the inorganic oxide fine particle, magnesium oxide, silicon oxide, aluminum oxide, titanium oxide, zirconium oxide, vanadium oxide, molybdenum oxide, tungsten oxide, tin oxide, zinc oxide, microporous three-dimensional aluminum silicate such as zeolite, a layered silicate mineral such as montmorillonite, beidellite, saponite, steven site, or hectorite, or the like is used. The inorganic oxide fine particle may be used alone or a plurality of inorganic oxide fine particles may be used in combination. In consideration of the dispersibility into the catalyst layer, the use of fine particles is preferable and the use of silicon oxide is preferable because of the availability. The average particle size of the inorganic oxide fine particles is preferably 3 nm or more and 3000 nm or less. An average particle size of the inorganic oxide fine particles of less than 3 nm leads to a difficulty in handling, and an average particle size of the inorganic oxide fine particles exceeding 3000 nm may cause a decrease in proton conductivity of the catalyst layer.

[0047] The polymer material which binds the catalyst support supporting the reduction catalyst and the inorganic oxide fine particle is desirably a water-insoluble polymer material which can maintain a catalyst layer structure even in a wet environment. As the polymer materials, a fluorine-based resin such as perfluoroalkoxyalkane (PFA), perfluoroethylene propene copolymer (FEP), polytetrafluoroethylene (PTFE), ethylene-tetrafluoroethylene copolymer (ETFE), polyvinylidene fluoride (PVDF), polychlorotrifluoroethylene (PCTFE), or ethylene-chlorotrifluoroethylene copolymer (ECTFE), polystyrene, polyvinyl butyral, poly(4-vinylpyridine), or the like is used. The polymer material as a binding agent may have ion conductivity. Examples of the polymer material having ion conductivity include Nafion (registered trademark) being a fluorocarbon resin made by sulfonating and polymerizing tetrafluoroethylene of DuPont Inc., Sustainion (registered trademark) of Dioxide Materials Inc., PiperION (registered trademark) of Versogen Inc., and so on.

[0048] A mass (Wca-p) of the polymeric material in the cathode catalyst layer is preferably in a range of 0.3 or more and 4.0 or less with respect to the total (Wca-c + Wca-i) of a mass (Wca-c) of the catalyst support and a mass (Wca-i) of the inorganic oxide fine particle. Further, the mass (Wca-c) of the catalyst support is preferably in a range of 1.0 or more and 10.0 or less with respect to the mass (Wca-i) of the inorganic oxide fine particle. With these ranges, it is possible to promote the production of ammonia without causing a decrease in proton conductivity nor electronic conductivity of the catalyst layer.

[0049] The catalyst layer may contain an ionic liquid. Arranging the ionic liquid on the catalyst support surface of the

catalyst layer to suppress adhesion of excessive moisture provides an effect of decreasing the occurrence of hydrogen by reduction of water and promoting the ammonia production reaction. For the ionic liquid contained in the reduction catalyst, the same one used in the above electrolytic solution can be used.

[0050] As the diaphragm 4 provided between the first reaction tank 2 as the cathode chamber and the second reaction tank as the anode chamber in the electrochemical reaction unit 5, a film which can selectively allow anion or cation to flow therethrough is used. The film constituting the diaphragm 4 is composed of a composite containing the inorganic oxide fine particle and the polymeric material binding the inorganic oxide fine particle. The inorganic oxide fine particle in the composite film constituting the diaphragm 4 functions as an ion conductor inside the diaphragm 4 and undertakes a role of conducting and supplying ions required for the reaction of the ammonia production catalyst. When the hydrogen ion concentration in the electrolytic solution is 7 or less ($pH \leq 7$), hydrogen ions (H^+) are supplied to the ammonia production catalyst, whereas when the hydrogen ion concentration in the electrolytic solution is greater than 7 ($pH > 7$), hydroxide ions (OH^-) are supplied to the ammonia production catalyst. These can realize the function of the diaphragm 4 in the electrochemical reaction unit 5. In addition, the composite containing the inorganic oxide fine particle and the polymeric material can decrease the permeability of liquid such as the electrolytic solution and suppress the occurrence of a flooding phenomenon on the reduction electrode 14 side. Accordingly, it becomes possible to improve the production efficiency and the recovery efficiency of the electrolysis product such as ammonia on the reduction electrode 14 side.

[0051] As the inorganic oxide fine particle constituting the diaphragm 4, magnesium oxide, silicon oxide, aluminum oxide, titanium oxide, zirconium oxide, vanadium oxide, molybdenum oxide, tungsten oxide, tin oxide, zinc oxide, microporous three-dimensional aluminum silicate such as zeolite, a layered silicate mineral such as montmorillonite, beidellite, saponite, steven site, or hectorite, or the like is used. The inorganic oxide fine particle may be used alone or a plurality of inorganic oxide fine particles may be used in combination. In consideration of the dispersibility into the diaphragm 4, the use of fine particles is preferable and the use of silicon oxide is preferable because of the availability. The average particle size of the inorganic oxide fine particles is preferably 3 nm or more and 3000 nm or less. An average particle size of the inorganic oxide fine particles of less than 3 nm leads to a difficulty in handling, and an average particle size of the inorganic oxide fine particles exceeding 3000 nm may cause a decrease in proton conductivity of the diaphragm 4.

[0052] The polymeric material which binds the inorganic oxide fine particle in the diaphragm 4 is desirably a water-insoluble polymer material which can maintain a diaphragm structure even in a wet environment. As the polymer material, a fluorine-based resin such as perfluoroalkoxyalkane (PFA), perfluoroethylene propene copolymer (FEP), polytetrafluoroethylene (PTFE), ethylene-tetrafluoroethylene copolymer (ETFE), polyvinylidene fluoride (PVDF), polychlorotrifluoroethylene (PCTFE), or ethylene-chlorotrifluoroethylene copolymer (ECTFE), polystyrene, polyvinyl butyral, poly(4-vinylpyridine), or the like is used.

[0053] Since the diaphragm 4 has ion conductivity, the polymeric material which binds the inorganic oxide fine particle also preferably has ion conductivity. As the polymeric material which has ion conductivity, for example, an ion exchange membrane such as NEOSEPTA (registered trademark) of ASTOM Corporation, Selemion (registered trademark) of Asahi Glass Co., Ltd., Aciplex (registered trademark) of Asahi Kasei Corp., Fumasep (registered trademark) and fumapem (registered trademark) of Fumatech GmbH., Nafion (registered trademark) being a fluorocarbon resin made by sulfonating and polymerizing tetrafluoroethylene of DuPont Inc., lewabrane (registered trademark) of LANXESS Co. Ltd., IONSEP (registered trademark) of IONTECH Inc., Mustang (registered trademark) of PALL Corp., ralex (registered trademark) of mega Corp., Gore-Tex (registered trademark) of Gore-Tex Inc., Sustainion (registered trademark) of Dioxide Materials Inc., PiperION (registered trademark) of Versogen Inc., or the like can be used.

[0054] The diaphragm 4 may contain, as the inorganic oxide fine particle and the polymeric material, for example, a silicone resin, a fluorine-based resin such as perfluoroalkoxyalkane (PFA), perfluoroethylene propene copolymer (FEP), polytetrafluoroethylene (PTFE), ethylene-tetrafluoroethylene copolymer (ETFE), polyvinylidene fluoride (PVDF), polychlorotrifluoroethylene (PCTFE), or ethylene-chlorotrifluoroethylene copolymer (ECTFE), a ceramic porous particle, packing filled with a glass filter or agar, an insulating porous body such as zeolite or oxide, or the like, in addition to the ion-exchange resin. The diaphragm 4 is preferably a hydrophilic porous film.

[0055] A mass (Wf-p) of the polymeric material in the diaphragm 4 is preferably in a range of 0.1 or more and 0.7 or less with respect to the mass (Wf-i) of the inorganic oxide fine particle. The thickness of the diaphragm 4 is preferably 10 μm or more and 500 μm or less, more preferably 50 μm or more and 300 μm or less, and furthermore preferably 100 μm or more and 200 μm or less. The thickness in the range can promote the production of ammonia without causing a decrease in proton conductivity of the diaphragm 4.

[0056] In the nitrogen electrolysis device 1 illustrated in FIG. 1, the nitrogen supply unit 7 is a unit which supplies gaseous nitrogen to the first reaction tank (reduction reaction electrolytic tank) 2, and includes the nitrogen supply device 6. As the nitrogen to be supplied from the nitrogen supply device 6, for example, nitrogen in the air is used, but is not limited to this. Since about 21% of oxygen is contained in the air, it is preferable to separate oxygen in advance and then take out nitrogen. In the case of using nitrogen in the air, an oxygen separation device which separates oxygen in the air and takes out nitrogen is used for the nitrogen supply device 6. As a separation method of oxygen in the air in the oxygen separation

device, for example, the cryogenic separation method of separating oxygen by utilizing a difference in boiling point, the adsorption separation method utilizing a difference in adsorbing characteristics with respect to gas molecules of a zeolite-based adsorbent, the membrane separation method of separating oxygen by utilizing the fact that the speed of permeating a membrane differs depending on gas molecules, or the like is used and can be appropriately selected according to the cost and device scale, and the separation method is not particularly limited. The nitrogen supply unit 7 further includes a humidifying device 18 that humidifies nitrogen taken out of the air. It is preferable to supply the humidified nitrogen to the first reaction tank 2.

[0057] A nitrogen gas containing ammonia and a hydrogen gas produced by a side reaction are discharged from the first reaction tank 2, and part of the electrolytic solution passing through the diaphragm (electrolyte membrane) 4 is discharged from the anode 15. A discharge pipe of the first reaction tank 2 is connected to the ammonia collection unit 9. The ammonia collection unit 9 is a unit that collects ammonia discharged from the first reaction tank 2 and includes the ammonia collection device 8. The ammonia collection device 8 is not particularly limited and, for example, a device which selectively collects ammonia by bringing the exhaust gas into contact with an aqueous solution (collection solution) with a pH of 0 to 7 for absorbing ammonia is used. The ammonia collection device 8 can simultaneously separate byproduct hydrogen and unreacted nitrogen contained in the exhaust gas.

[0058] The ammonia collected by the ammonia collection device 8 and the part of the electrolytic solution passing through the diaphragm (electrolyte membrane) 4 from the anode 15 are contained in the collection solution and thus sent to a first separation device 19 which separates ammonia from the collection solution. For the first ammonia separation device 19, for example, the distillation method or the cryogenic separation method of separating ammonia by utilizing the difference in boiling point, the adsorption separation method utilizing the difference in adsorbing characteristics with respect to gas molecules of the zeolite-based adsorbent, the membrane separation method of separating ammonia by utilizing the fact that the speed of permeating the membrane differs depending on the gas molecules, or the like is applied. The first ammonia separation device 19 can be appropriately selected according to the cost and device scale and is not particularly limited. The first ammonia separation device 19 is provided with a pipe for recovering the ammonia separated from the collection solution.

[0059] In the case of separating ammonia from the collection solution by distillation, a distillation column is used as the first ammonia separation device 19. The distillation column is configured to separate ammonia having a boiling point lower than water used as at least part of the collection solution. In the distillation column, ammonia is separated by distillation by the conventional method from the supplied collection solution. Concretely, ammonia is discharged from a pipe at a column top part of the distillation column by subjecting the collection solution to reduced-pressure distillation under a reduced pressure of 10 Torr to 120 Torr (1333 to 15999 Pa). The ammonia discharged from the pipe is recovered into a not-illustrated tank or the like.

[0060] For the separation of ammonia, the stripping method of bringing the collection solution into contact with vapor and moving the ammonia in the collection solution to the vapor to recover the ammonia may be used. In this case, the first ammonia separation device 19 includes a stripping column whose inside is partitioned by a porous plate and is configured to make the supplied collection solution flow from an upper tier to a lower tier of the stripping column. The vapor flows from the lower tier to the upper tier and rises in the solution dammed by the porous plate. Because of the contact of the collection solution with the vapor, the ammonia in the collection solution vaporizes and moves into the vapor and is thereby discharged from the pipe at the column top part. Besides, in the case of using a carbonate aqueous solution as the collection solution, the ammonia in the collection solution can be converted to ammonium hydrogen carbonate, which can be pyrolyzed by a pyrolyzer to separate and recover ammonia and carbon dioxide. The moisture separated in the ammonia separation device 19 and the part of the electrolytic solution passing through the diaphragm (electrolyte membrane) 4 from the anode 15 are sent again to an electrolytic solution storage tank 21 and utilized again as the anode electrolytic solution.

[0061] The second reaction tank 3 is connected to the electrolytic solution circulation unit 13. The electrolytic solution circulation unit 13 is a unit that circulates the electrolytic solution in the circulation pipe 12 so that the electrolytic solution containing the produced ammonia is taken from the second reaction tank 3 to the outside and the electrolytic solution is supplied again to the second reaction tank 3. The circulation pipe 12 is provided with a liquid feed pump 20 for circulating the electrolytic solution, and an electrolytic solution storage tank 21 for storing the electrolytic solution and regulating the electrolyte concentration, pH, and so on. The electrolytic solution circulation unit 13 is configured to circulate the electrolytic solution between the second reaction tank 3 and the electrolytic solution storage tank 21 by the liquid feed pump 20.

[0062] Though the liquid feed pump 20 is provided in the circulation pipe 12 which sends the electrolytic solution from the electrolytic solution storage tank 21 to the second reaction tank 3 in FIG. 1, the liquid feed pump 20 may be provided in the circulation pipe 12 which sends the electrolytic solution from the second reaction tank 3 to the electrolytic solution storage tank 21. The electrolytic solution circulation unit 13 preferably includes an exhaust unit which exhausts excessive nitrogen that has not dissolved in the electrolytic solution and gas that has been generated by the oxidation reaction. As the exhaust unit, for example, a pipe provided with a valve is used and is provided, for example, in the electrolytic solution storage tank 21. The electrolytic solution storage tank 21 functions as a gas-liquid separation tank, where oxygen (O_2) generated by the

oxidation reaction is separated from the electrolytic solution.

[0063] The ammonia separation unit 11 is a unit which recovers ammonia (NH_3) that is a reduced substance of nitrogen, from the electrolytic solution. The ammonia separation unit 11 includes a second separation device 10 which separates ammonia from the electrolytic solution, a three-way valve 22 which takes out at least part of the electrolytic solution circulating in the circulation pipe 12, a pipe 23 which sends the electrolytic solution taken out of the three-way valve 22 to the second separation device 10, and a pipe 24 which sends the electrolytic solution from which ammonia has been separated in the second separation device 10 to the electrolytic solution storage tank 21. The three-way valve 22 is provided in the circulation pipe 12, and the ammonia separation unit 11 is connected to the electrolytic solution circulation unit 13 through the three-way valve 22. The taking-out of the electrolytic solution circulating in the circulation pipe 12 may be implemented not by using the three-way valve 22 provided in the circulation pipe 12 but by connecting a pipe having a valve to the electrolytic solution storage tank 21, and its configuration is not particularly limited. The second ammonia separation device 10 uses a similar separation method as the first ammonia separation device 19, and has a similar configuration.

[0064] Next, an ammonia manufacturing process using the above nitrogen electrolysis device (ammonia manufacturing apparatus) will be explained. First, as an initial stage, a humidified nitrogen gas is supplied to the first reaction tank 2. The electrolytic solution is supplied into the second reaction tank 3 through the circulation pipe 12. In this state, electric power is supplied from the external electrode 17 to the reduction electrode 14 and the oxidation electrode 15.

[0065] The external electrode 17 may be an ordinary commercial power supply, a battery, or the like, or a power supply that converts renewable energy to electric energy and supplies it. Examples of the power supply include a power supply that converts kinetic energy or potential energy such as wind power, water power, geothermal power, or tidal power into electric energy, a power supply such as a solar cell having a photoelectric conversion element that converts light energy into electric energy, a power supply such as a fuel cell or a storage battery that converts chemical energy into electric energy, an apparatus that converts vibrational energy such as sound into electric energy, and so on. The photoelectric conversion element has a function of performing charge separation by energy of emitted light such as sunlight. Examples of the photoelectric conversion element include a pin-junction solar cell, a pn-junction solar cell, an amorphous silicon solar cell, a multijunction solar cell, a single-crystal silicon solar cell, a polycrystalline silicon solar cell, a dye-sensitized solar cell, an organic thin-film solar cell, a perovskite solar cell, and the like.

[0066] By supplying electric power from the external electrode 17 to the reduction electrode 14 and the oxidation electrode 15, an oxidation reaction of water (H_2O) or hydroxide ions (OH^-) in the electrolytic solution electrochemically occurs at the oxidation electrode 15. For example, when the hydrogen ion concentration in the electrolytic solution is 7 or less (pH $\leq$ 7), H_2O is oxidized to produce O_2 and H^+ based on Formula (1) below. When the hydrogen ion concentration in the electrolytic solution is greater than 7 (pH > 7), OH^- is oxidized to produce O_2 and H_2O based on Formula (2) below.

$$3H_2O \rightarrow 3/2O_2 + 6H^+ + 6e^- \ldots \quad (1)$$

$$6OH^- \rightarrow 3/2O_2 + 3H_2O + 6e^- \ldots \quad (2)$$

[0067] In the first reaction tank 2, nitrogen (N_2) is reduced by the ammonia-producing catalyst to produce ammonia (NH_3). The ammonia-producing catalyst is as explained above. N_2 is reduced by conducting ion species in the diaphragm 4 to produce ammonia (NH_3) based on Formula (3) or Formula (4) below.

$$N_2 + 6H_2O + 6e^- \rightarrow 2NH_3 + 6OH^- \ldots \quad (3)$$

$$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3 \ldots \quad (4)$$

[0068] The gas containing NH_3 produced by the N_2 reduction explained above is sent through a pipe to the collection device 8, where ammonia is selectively collected by bringing the exhaust gas into contact with the aqueous solution (collection solution) with a pH of 0 to 7, as explained above. At the same time, the byproduct hydrogen and unreacted nitrogen contained in the exhaust gas are separated. The collection solution containing ammonia is sent to the first ammonia separation device 19, where ammonia is separated from the collection solution.

[0069] Part of NH_3 produced by the N_2 reduction is sent through the diaphragm 4 to the second reaction tank 3 and dissolved in the electrolytic solution. The electrolytic solution containing NH_3 is sent through the circulation pipe 12 to the electrolytic solution storage tank 21 where oxygen (O_2) is separated therefrom, and then sent again to the second reaction tank 3. By circulating the electrolytic solution in the circulation pipe 12, an ammonia concentration in the electrolytic solution increases. By sending at least part of the electrolytic solution with increased ammonia concentration to the second ammonia separation device 10 through the three-way valve 22, ammonia is separated from the electrolytic solution.

[0070] The supply of the electrolytic solution containing ammonia to the second ammonia separation device 10 may be performed continuously from the start of operation of the device but is preferably intermittently performed at the point in

time when the concentration of ammonia contained in the electrolytic solution becomes high enough. In other words, when the concentration of ammonia contained in the electrolytic solution is low, the energy to be supplied to recover ammonia from the electrolytic solution becomes larger than the energy amount stored in ammonia, leading to an increase in manufacturing cost of ammonia. Regarding this point, the electrolytic solution is circulated by the circulation pipe 12 through the second reaction tank 3 and the electrolytic solution storage tank 21, thereby making it possible to obtain the electrolytic solution containing ammonia at high concentration. It is preferable to send the electrolytic solution containing ammonia at high concentration to the second ammonia separation device 10. This makes it possible to recover ammonia being a reduction product of N_2 with high efficiency. To improve the recovery efficiency of ammonia, it is preferable to send the electrolytic solution containing ammonia at a concentration of 0.01 to 50 mass% to the ammonia separation device 10.

[0071] Next, an additional configuration example, modification example, and so on of the nitrogen electrolysis device 1 in the embodiment will be explained. The second reaction tank 3 may be provided with a circulation mechanism such as a pump. Promoting the circulation of the electrolytic solution by the circulation mechanism can improve the circulation of ions (H^+ and OH^-) between the second reaction tank 3 for the oxidation reaction and the first reaction tank 2 for the reduction reaction. The first and second reaction tanks 2, 3 may be provided with flow paths and may be provided with a plurality of circulation mechanisms. Further, a plurality of (three or more) reaction tank flow paths may be provided to decrease the diffusion of ions and to more efficiently circulate the ions. The circulation mechanism creates the flow of liquid to make it possible to suppress stay of generated bubbles on electrode surfaces and surfaces of the reaction tanks to promote the reactions.

[0072] The first and second reaction tanks 2, 3 may be provided with temperature-regulating mechanisms that regulate the temperature of the electrolytic solution. By controlling the temperature using the temperature-regulating mechanisms, it is possible to control the catalytic performance. For example, by making the temperature of a reaction system uniform, the performance of the catalyst can be stabilized. Further, a temperature increase can also be prevented for system stabilization. The reaction temperature in the electrochemical reaction cell 5 can be appropriately selected in a range of 5 to 95°C in consideration of the electrolytic solution being an aqueous solution, reaction efficiency, and economic efficiency. Preferably, the reaction temperature may be near room temperature (10 to 60°C).

[0073] The electrochemical reaction cell 5 can increase the reaction area and obtain more reaction current by making the electrodes more porous. The electrochemical reaction cell 5 may have an electrode structure with a diaphragm sandwiched between a porous oxidation electrode and a porous reduction electrode. In other words, in the electrochemical reaction cell 5 illustrated in FIG. 2, the porous oxidation electrode and the porous reduction electrode are arranged in contact with both surfaces of the diaphragm, respectively. The electrolytic solution is supplied to a surface of the porous oxidation electrode opposite to the surface in contact with the diaphragm. The ammonia-producing catalyst is arranged on a surface of the porous reduction electrode in contact with the diaphragm, and nitrogen is supplied to a surface of the porous reduction electrode opposite to the surface in contact with the diaphragm. The electrochemical reaction cell 5 may have a nitrogen supply pipe that supplies nitrogen to the ammonia-producing catalyst through the porous reduction electrode and the porous oxidation electrode. A pathway through which nitrogen flows may be provided with a flow path. By providing a plurality of (three or more) gas flow paths, nitrogen can be distributed uniformly to the porous reduction electrode.

[0074] The electrochemical reaction cell 5 may have the electrolytic solution between the porous reduction electrode and the diaphragm. In other words, the electrochemical reaction cell 5 illustrated in FIG. 3 can be supplied with nitrogen from a surface of the reduction electrode 14 opposite to the ammonia-producing catalyst. Thus, the structure of the electrochemical reaction cell 5 can be variously modified.

EXAMPLES

[0075] Next, examples and their evaluation results will be explained.

[Fabrication of the cathode]

[0076] The cathode was fabricated by spray coating of catalyst ink on carbon paper formed with a carbon particle layer (MPL layer). The catalyst ink used for the cathode was prepared using ketjen black (manufactured by LION SPECIALTY CHEMICALS CO., LTD., EC600JD, BET specific surface area: 1270 m^2/g) 0.25 g, silica 0.05 g, and PTFE 0.3 g as a support for the molybdenum complex, and 2-propanol 50 mL and pure water 50 mL as a dispersion medium. The catalyst ink was prepared by mixing ketjen black, silica, PTFE, and 2-propanol in a glass vial bottle and dispersing them for 20 minutes using an ultrasonic homogenizer. Next, a catalyst layer was formed by spray coating of the catalyst ink on carbon paper (manufactured by Avcarb Co., Ltd., MB-30 (product name)) which was fixed to a metal plate and heated to 90°C. The catalyst layer was applied on the MPL layer side. Amounts of ketjen black, silica, and PTFE per 1 cm^2 of the coated surface were 1.8 mg, 0.4 mg, and 2.1 mg, respectively. The electrode was baked at 380°C in an argon atmosphere for one hour and thereby bonded. Next, the electrode formed with the catalyst layer was immersed in a catalyst solution (a solution in which

1 mg of molybdenum complex was dissolved in 10 mL of methanol) in which a molybdenum triiodide complex (as ligand, 1,3-bis(ditertiarybutylphosphinomethylbenzoimidazole-2-ylidene) being a PCP ligand) was dissolved in methanol, at room temperature in an argon atmosphere for one hour. The electrode was then air-dried under argon flow to form into a cathode (20 mm × 20 mm square). The ketjen black of the cathode adsorbed 0.1 mg of molybdenum complex.

[Fabrication of the anode]

[0077] The anode was made of Ti in a mesh structure by an etching method, and used by forming iridium oxide as an oxidation catalyst on a wire mesh (20 mm × 20 mm square) with an increased surface area.

[Fabrication of a membrane electrode assembly and N_2 electrolysis cell]

[0078] A membrane electrode assembly (catalyst area of 400 mm^2) was prepared by sandwiching a Sustainion (registered trademark) membrane (25 mm × 25 mm square) of Dioxide Materials Inc. as the diaphragm between the anode and the cathode to stack them. Note that a cathode catalyst layer and an anion exchange membrane were placed in contact with each other. The membrane electrode assembly was sandwiched between titanium flow paths (serpentine, a land width of 0.4 mm, a flow path width of 1.5 mm, a flow path depth of 1 mm) through a Teflon gasket to assemble the N_2 electrolysis cell.

[Constant potential electrolysis measurement (ammonia production experiment)]

[0079] A 0.1 M potassium sulfate solution was supplied as the electrolytic solution to an anode flow path of the N_2 electrolysis cell at 1 mL/min. The pH of the electrolytic solution was 7. On the other hand, 100% N_2 gas saturated and humidified at room temperature was supplied to a cathode flow path at 40 mL/min. A power supply device (Solar TRON Cell Test System, manufactured by TOYO Corporation) was connected from outside the cathode flow path and the anode flow path, and a voltage of 3.0 V was applied for one hour. Reduction products generated from the cathode of the N_2 electrolysis cell were analyzed. Liquid and gas discharged from the cathode flow path were collected in a 10 mM sulfuric acid aqueous solution as an ammonia collection solution, and ammonia was quantified. In addition, gas after ammonia collection was sampled and hydrogen was quantified by gas chromatography (manufactured by Varian Medical Systems Inc., Micro GC CP4900).

[Ammonia quantification method (indophenol method)]

[0080] The quantification of ammonia was performed by an indophenol method. An analytical procedure of the indophenol method is shown below. After adding 5 ml of coloring solution (1) (5 g of phenol and 25 mg of sodium nitroprusside ($Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$) were added to pure water into 500 ml) to 2.5 ml of ammonia collection solution and mixing them, 5 ml of coloring solution (2) (2.5 g of sodium hydroxide and 4.2 ml of sodium hypochlorite were added to pure water into 500 ml) was added and mixed. The solution was kept stand at room temperature for 30 minutes or more. The solution was subjected to measurement of absorbance due to indophenol derivatives at around 640 nm in an ultraviolet-visible absorption spectrophotometer (manufactured by Shimadzu Corporation, UV-2500PC), to quantify ammonia.

[0081] Faraday efficiency was calculated based on the current consumed for the cathode reduction reaction and quantitative analysis of the reduction products. The Faraday efficiency is expressed as a percentage of the amount of electricity required to produce the reduction products relative to the amount of electricity input. The Faraday efficiency of each reduction product analyzed was used as product selectivity (%). In the N_2 electrolysis cell prepared by the above method, the selectivity of ammonia was 1.00%.

(Example 2)

[0082] The ink composition in the cathode catalyst layer was changed and a cathode containing 1.8 mg of ketjen black, 0.4 mg of silica, and 5.0 mg of PTFE per 1 cm^2 of the coated surface was fabricated. A N_2 electrolysis cell was fabricated in the same manner as in Example 1, except that the cathode was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 0.77%.

(Example 3)

[0083] The ink composition in the cathode catalyst layer was changed and a cathode containing 1.8 mg of ketjen black, 0.4 mg of silica, and 0.9 mg of PTFE per 1 cm^2 of the coated surface was fabricated. A N_2 electrolysis cell was fabricated in

the same manner as in Example 1, except that the cathode was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 0.81%.

(Example 4)

[0084] The ink composition in the cathode catalyst layer was changed and a cathode containing 1.8 mg of ketjen black, 0.2 mg of silica, and 2.0 mg of PTFE per 1 cm^2 of the coated surface was fabricated. A N_2 electrolysis cell was fabricated in the same manner as in Example 1, except that the cathode was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 1.12%.

(Example 5)

[0085] The ink composition in the cathode catalyst layer was changed and a cathode containing 1.8 mg of ketjen black, 0.7 mg of silica, and 1.5 mg of PTFE per 1 cm^2 of the coated surface was fabricated. A N_2 electrolysis cell was fabricated in the same manner as in Example 1, except that the cathode was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 0.91%.

(Example 6)

[0086] The ink composition in the cathode catalyst layer was changed and a cathode containing 3.5 mg of ketjen black, 0.4 mg of silica, and 3.9 mg of PTFE per 1 cm^2 of the coated surface was fabricated. A N_2 electrolysis cell was fabricated in the same manner as in Example 1, except that the cathode was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 0.22%.

(Example 7)

[0087] The ink composition in the cathode catalyst layer was changed and a cathode containing 0.4 mg of ketjen black, 0.4 mg of silica, and 0.7 mg of PTFE per 1 cm^2 of the coated surface was fabricated. A N_2 electrolysis cell was fabricated in the same manner as in Example 1, except that the cathode was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 0.30%.

(Example 8)

[0088] A N_2 electrolysis cell was fabricated in the same manner as in Example 1, except that the silica in the cathode catalyst layer ink was changed to titania. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 0.91%.

(Example 9)

[0089] A N_2 electrolysis cell was fabricated in the same manner as in Example 1, except that the silica in the cathode catalyst layer ink was changed to alumina. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 0.85%.

(Example 10)

[0090] A N_2 electrolysis cell was fabricated in the same manner as in Example 1, except that the silica in the cathode catalyst layer ink was changed to zinc oxide. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 0.67%.

(Example 11)

[0091] A N_2 electrolysis cell was fabricated in the same manner as in Example 1, except that the silica in the cathode catalyst layer ink was changed to zeolite A-4. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 0.73%.

(Example 12)

[0092] A N_2 electrolysis cell was fabricated in the same manner as in Example 1, except that the silica in the cathode

catalyst layer ink was changed to hectorite. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 0.75%.

(Comparative example 1)

[0093] The ink composition in the cathode catalyst layer was changed and a cathode containing 1.8 mg of ketjen black, 0.4 mg of silica, and 0.2 mg of PTFE per 1 cm^2 of the coated surface was fabricated. A N_2 electrolysis cell was fabricated in the same manner as in Example 1, except that the cathode was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 0.12%.

(Comparative example 2)

[0094] The ink composition in the cathode catalyst layer was changed and a cathode containing 1.8 mg of ketjen black, 0.4 mg of silica, and 19.1 mg of PTFE per 1 cm^2 of the coated surface was fabricated. A N_2 electrolysis cell was fabricated in the same manner as in Example 1, except that the cathode was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 0.09%.

(Comparative example 3)

[0095] The ink composition in the cathode catalyst layer was changed and a cathode containing 0.2 mg of ketjen black, 0.4 mg of silica, and 0.6 mg of PTFE per 1 cm^2 of the coated surface was fabricated. A N_2 electrolysis cell was fabricated in the same manner as in Example 1, except that the cathode was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 0.01%.

(Comparative example 4)

[0096] The ink composition in the cathode catalyst layer was changed and a cathode containing 4.2 mg of ketjen black, 0.4 mg of silica, and 3.9 mg of PTFE per 1 cm^2 of the coated surface was fabricated. A N_2 electrolysis cell was fabricated in the same manner as in Example 1, except that the cathode was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 0.02%.

[0097] According to Examples 1 to 12 and Comparative examples 1 to 4, it is preferable that the mass (Wca-p) of the polymeric material in the cathode catalyst layer is in a range of 0.3 to 4.0 with respect to the total (Wca-c + Wca-i) of the mass (Wca-c) of the catalyst support and the mass (Wca-i) of the inorganic oxide fine particle. Further, it is preferable that the mass (Wca-c) of the catalyst support is in a range of 1.0 to 10 with respect to the mass (Wca-i) of the inorganic oxide fine particle.

(Example 13)

[Fabrication of the cathode]

[0098] The cathode was fabricated by spray coating of catalyst ink on carbon paper formed with a carbon particle layer (MPL layer). The catalyst ink used for the cathode was prepared using ketjen black (manufactured by LION SPECIALTY CHEMICALS CO., LTD., EC600JD, BET specific surface area: 1270 m^2/g) 0.3 g and PTFE 0.3 g as a support for the molybdenum complex, and 2-propanol 50 mL and pure water 50 mL as a dispersion medium. The catalyst ink was prepared by mixing ketjen black, PTFE, and 2-propanol in a glass vial bottle and dispersing them for 20 minutes using an ultrasonic homogenizer. Next, a catalyst layer was formed by spray coating of the catalyst ink on carbon paper (manufactured by Avcarb Co., Ltd., MB-30 (product name)) which was fixed to a metal plate and heated to 90°C. The catalyst layer was applied on the MPL layer side. Amounts of ketjen black and PTFE per 1 cm^2 of the coated surface were 2.1 mg and 2.1 mg, respectively. The electrode was baked at 380°C in an argon atmosphere for one hour and thereby bonded. Next, the electrode formed with the catalyst layer was immersed in a catalyst solution (a solution in which 1 mg of molybdenum complex was dissolved in 10 mL of methanol) in which a molybdenum triiodide complex (as ligand, 1,3-bis(ditertiarybutylphosphinomethylbenzoimidazole-2-ylidene) being a PCP ligand) was dissolved in methanol, at room temperature in an argon atmosphere for one hour. The electrode was then air-dried under argon flow to form into a cathode (20 mm $\times$ 20 mm square). The activated carbon of the cathode adsorbed 0.1 mg of molybdenum complex.

[Fabrication of the electrolyte membrane (diaphragm)]

[0099] The electrolyte membrane was fabricated by spray coating of electrolyte ink on a porous polymer base material.

The electrolyte ink used for the electrolyte membrane was prepared using silica 0.7 g, Nafion solution (2-propanol solution with a resin solid content concentration of 5%) 6g, and 2-propanol 15 mL as a dispersion medium. The electrolyte ink was prepared by mixing silica, Nafion solution, and 2-propanol in a glass vial bottle and dispersing them for 20 minutes using an ultrasonic homogenizer. Next, an electrolyte membrane was formed by spray coating of the electrolyte ink on a porous substrate of polyethersulfone (manufactured by GVS) which was fixed to a metal plate and heated to 90°C. Amounts of silica and Nafion solution per 1 cm^2 of the coated surface were 5 mg and 2 mg, respectively, and the thickness was 130 μm. This was immersed in boiling water for 15 min, and subjected to a wet treatment to form into an electrolyte membrane (25 mm × 25 mm square).

[Fabrication of the membrane electrode assembly and N_2 electrolysis cell]

[0100] A membrane electrode assembly (catalyst area of 400 mm^2) was prepared by sandwiching an electrolyte membrane (diaphragm) between the anode and the cathode to stack them. Note that the cathode catalyst layer and the electrolyte membrane were arranged in contact with each other. The membrane electrode assembly was sandwiched between titanium flow paths (serpentine, a land width of 0.4 mm, a flow path width of 1.5 mm, a flow path depth of 1 mm) through a Teflon gasket to assemble the N_2 electrolysis cell. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 1. As a result, the selectivity of ammonia was 2.00%.

(Example 14)

[0101] The electrolyte ink composition was changed and an electrolyte membrane containing 6.4 mg of silica and 0.7 mg Nafion per 1 cm^2 of the coated surface was fabricated. A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the electrolyte membrane was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 11. As a result, the selectivity of ammonia was 1.77%.

(Example 15)

[0102] The electrolyte ink composition was changed and an electrolyte membrane containing 4.2 mg of silica and 2.8 mg Nafion per 1 cm^2 of the coated surface was fabricated. A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the electrolyte membrane was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 11. As a result, the selectivity of ammonia was 1.53%.

(Example 16)

[0103] The amount of electrolyte ink applied was changed to double and an electrolyte membrane containing 9.9 mg of silica and 4.2 mg Nafion per 1 cm^2 of the coated surface was fabricated. The thickness of the electrolyte was 250 μm. A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the electrolyte membrane was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 11. As a result, the selectivity of ammonia was 1.64%.

(Example 17)

[0104] The amount of electrolyte ink applied was changed to half and an electrolyte membrane containing 2.5 mg of silica and 1.1 mg Nafion per 1 cm^2 of the coated surface was fabricated. The thickness of the electrolyte was 60 μm. A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the electrolyte membrane was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 11. As a result, the selectivity of ammonia was 1.85%.

(Example 18)

[0105] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the silica in the electrolyte ink was changed to titania. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 1.91%.

(Example 19)

[0106] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the silica in the electrolyte ink was changed to zirconia. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same

manner as in Example 13. As a result, the selectivity of ammonia was 1.76%.

(Example 20)

[0107] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the silica in the electrolyte ink was changed to tin oxide. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 1.33%.

(Example 21)

[0108] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the silica in the electrolyte ink was changed to zeolite F-6. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 1.17%.

(Example 22)

[0109] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the silica in the electrolyte ink was changed to hectorite. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 2.54%.

(Example 23)

[0110] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the electrolytic solution was changed to 0.1M sulfuric acid aqueous solution. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 0.54%.

(Example 24)

[0111] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the electrolytic solution was changed to 0.1M sodium silicate. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 2.03%.

(Example 25)

[0112] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the cathode was changed to the cathode in Example 1. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 3.00%.

(Example 26)

[0113] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the cathode was changed to the cathode in Example 2. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 2.77%.

(Example 27)

[0114] A N_2 electrolysis cell was prepared in the same manner as in Example 13, except that the cathode was changed to the cathode in Example 3. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 2.81%.

(Example 28)

[0115] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the cathode was changed to the cathode in Example 4. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 2.12%.

(Example 29)

[0116] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the cathode was changed to the cathode in Example 5. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 2.91%.

(Example 30)

[0117] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the cathode was changed to the cathode in Example 6. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 2.22%.

(Example 31)

[0118] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the cathode was changed to the cathode in Example 7. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 2.30%.

(Example 32)

[0119] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the cathode was changed to the cathode in Example 8. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 2.91%.

(Example 33)

[0120] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the cathode was changed to the cathode in Example 9. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 2.85%.

(Example 34)

[0121] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the cathode was changed to the cathode in Example 10. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 2.67%.

(Example 35)

[0122] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the cathode was changed to the cathode in Example 11. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 2.73%.

(Example 36)

[0123] A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the cathode was changed to the cathode in Example 12. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 13. As a result, the selectivity of ammonia was 2.75%.

(Example 37)

[0124] A N_2 electrolysis cell was fabricated in the same manner as in Example 14, except that the cathode was changed to the cathode in Example 1. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 14. As a result, the selectivity of ammonia was 2.77%.

(Example 38)

[0125] A N_2 electrolysis cell was fabricated in the same manner as in Example 15, except that the cathode was changed to the cathode in Example 1. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same

manner as in Example 15. As a result, the selectivity of ammonia was 2.53%.

(Example 39)

[0126] A N_2 electrolysis cell was fabricated in the same manner as in Example 16, except that the cathode was changed to the cathode in Example 1. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 16. As a result, the selectivity of ammonia was 2.64%.

(Example 40)

[0127] A N_2 electrolysis cell was fabricated in the same manner as in Example 17, except that the cathode was changed to the cathode in Example 1. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 17. As a result, the selectivity of ammonia was 2.85%.

(Example 41)

[0128] A N_2 electrolysis cell was fabricated in the same manner as in Example 18, except that the cathode was changed to the cathode in Example 1. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 18. As a result, the selectivity of ammonia was 2.91%.

(Example 42)

[0129] A N_2 electrolysis cell was fabricated in the same manner as in Example 19, except that the cathode was changed to the cathode in Example 1. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 19. As a result, the selectivity of ammonia was 2.76%.

(Example 43)

[0130] A N_2 electrolysis cell was fabricated in the same manner as in Example 20, except that the cathode was changed to the cathode in Example 1. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 20. As a result, the selectivity of ammonia was 2.33%.

(Example 44)

[0131] A N_2 electrolysis cell was fabricated in the same manner as in Example 21, except that the cathode was changed to the cathode in Example 1. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 21. As a result, the selectivity of ammonia was 2.17%.

(Example 45)

[0132] A N_2 electrolysis cell was fabricated in the same manner as in Example 22, except that the cathode was changed to the cathode in Example 1. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 22. As a result, the selectivity of ammonia was 3.54%.

(Example 46)

[0133] A N_2 electrolysis cell was fabricated in the same manner as in Example 23, except that the cathode was changed to the cathode in Example 1. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 23. As a result, the selectivity of ammonia was 1.54%.

(Example 47)

[0134] A N_2 electrolysis cell was fabricated in the same manner as in Example 24, except that the cathode was changed to the cathode in Example 1. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 24. As a result, the selectivity of ammonia was 3.03%.

(Comparative example 5)

[0135] The electrolyte ink composition was changed and an electrolyte membrane containing 6.7 mg of silica and 0.4 mg Nafion per 1 cm^2 of the coated surface was fabricated. A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the electrolyte membrane was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 11. As a result, the selectivity of ammonia was 0.05%.

(Comparative example 6)

[0136] The electrolyte ink composition was changed and an electrolyte membrane containing 3.5 mg of silica and 3.5 mg Nafion per 1 cm^2 of the coated surface was fabricated. A N_2 electrolysis cell was fabricated in the same manner as in Example 13, except that the electrolyte membrane was changed. Using this N_2 electrolysis cell, the manufacture of ammonia was attempted in the same manner as in Example 11. As a result, the selectivity of ammonia was 0.33%.

[0137] According to Examples 13 to 46 and Comparative examples 5, 6, a mass (Wf-p) of the polymeric material in the diaphragm is preferably in a range of 0.1 to 0.7 with respect to the mass (Wf-i) of the inorganic oxide fine particle. The thickness of the diaphragm (electrolyte membrane) is preferably 10 to 500 μm, more preferably 50 to 300 μm, and furthermore preferably 100 to 200 μm. The thickness in the range can promote the production of ammonia without causing a decrease in proton conductivity of the diaphragm.

[0138] Note that the configurations of the above-explained embodiments are applicable in combination. Further, parts thereof are replaceable. While certain embodiments of the present invention have been described above, these embodiments have been presented by way of example only, and are not intended to limit the scope of the invention. Indeed, the novel embodiments described herein may be embodied in a variety of other forms; furthermore, various omissions, substitutions and changes in the form of the embodiments described herein may be made without departing from the spirit of the inventions. The accompanying claims and their equivalents are intended to cover such forms or modifications as would fall within the scope and spirit of the inventions.

Claims

1. An electrolysis device comprising an electrolysis cell, the electrolysis cell comprising: a cathode chamber in which a reduction electrode is arranged and to which a gaseous substance to be reduced is supplied; an anode chamber in which an oxidation electrode is arranged and to which a substance to be oxidized in a liquid state or in a state of vaporized liquid is supplied; and a diaphragm provided between the cathode chamber and the anode chamber, wherein
at least one of the reduction electrode and the diaphragm includes a composite containing at least an inorganic oxide fine particle and an organic polymer material which binds the inorganic oxide fine particle.

2. The device according to claim 1, wherein
the inorganic oxide fine particle includes at least one selected from the group consisting of magnesium oxide, silicon oxide, aluminum oxide, titanium oxide, zirconium oxide, vanadium oxide, molybdenum oxide, tungsten oxide, tin oxide, zinc oxide, aluminum silicate, and a layered silicate mineral.

3. The device according to claim 1 or claim 2, wherein
the organic polymer material includes at least one selected from the group consisting of perfluoroalkoxyalkane, perfluoroethylene propene copolymer, polytetrafluoroethylene, ethylene-tetrafluoroethylene copolymer, polyvinylidene fluoride, polychlorotrifluoroethylene, ethylene-chlorotrifluoroethylene copolymer, polystyrene, polyvinyl butyral, poly(4-vinylpyridine), and an ion-exchange resin.

4. The device according to any one of claim 1 to claim 3, wherein
the composite included in the reduction electrode further contains a reduction catalyst which reduces the substance to be reduced and a porous carbon material which supports the reduction catalyst, and the porous carbon material which supports the reduction catalyst is bound together with the inorganic oxide fine particle by the organic polymer material.

5. The device according to claim 4, wherein
a ratio of a mass of the organic polymer material in the composite to a total of a mass of the porous carbon material which supports the reduction catalyst and a mass of the inorganic oxide fine particle is in a range of 0.3 or more and 4.0 or less, and a ratio of the mass of the porous carbon material which supports the reduction catalyst to the mass of the inorganic oxide fine particle is in a range of 1.0 or more and 10.0 or less.

6. The device according to any one of claim 1 to claim 5, wherein
a mass of the organic polymer material in the composite included in the diaphragm to a mass of the inorganic oxide fine particle is in a range of 0.1 or more and 0.7 or less.

7. The device according to any one of claim 1 to claim 6, wherein
a thickness of the diaphragm is 10 μm or more and 500 μm or less.

8. The device according to any one of claim 1 to claim 7, wherein:

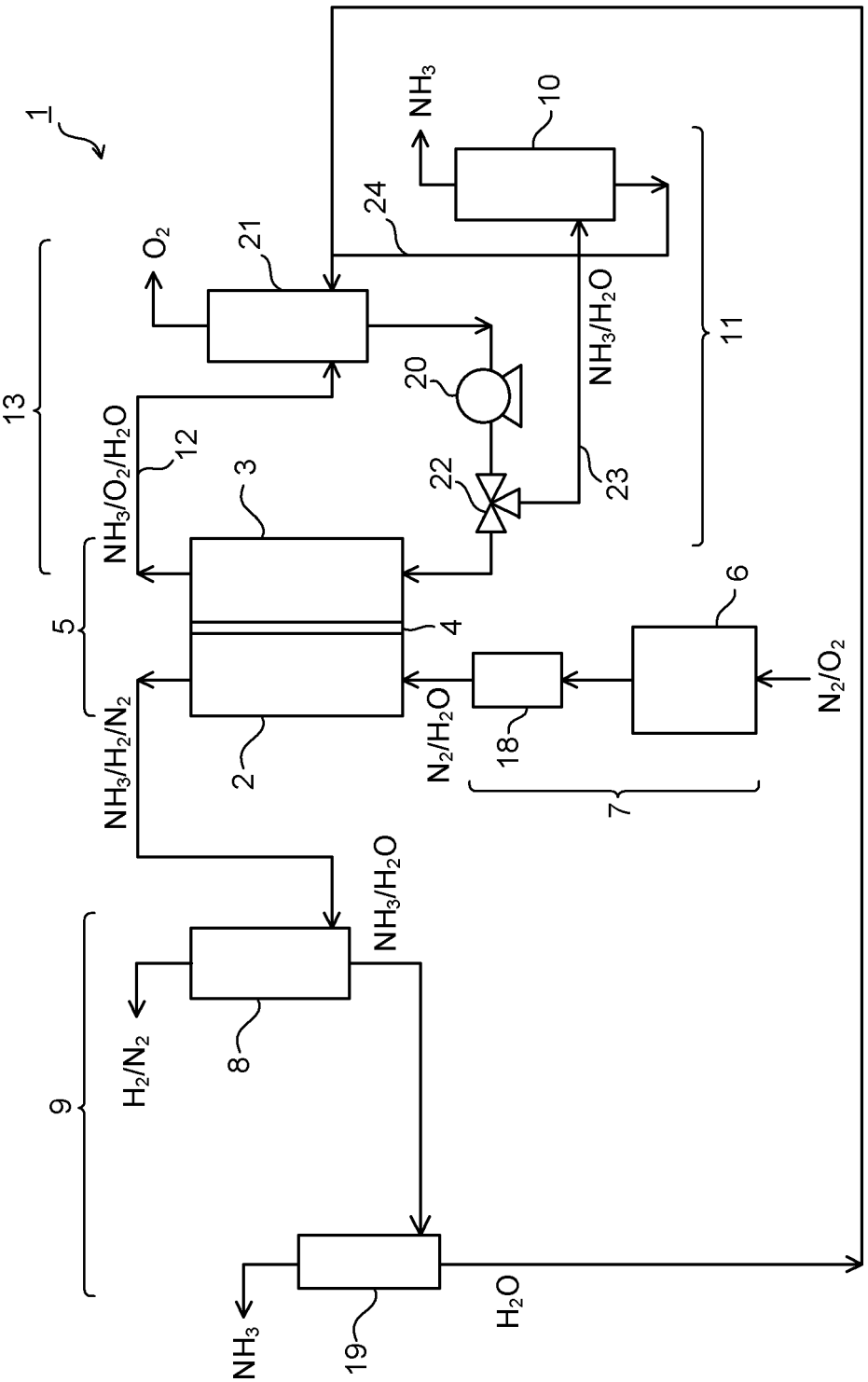
the electrolysis device is a nitrogen electrolysis device configured to reduce nitrogen to manufacture ammonia; and
the reduction electrode contains a molybdenum complex as a reduction catalyst.

9. The device according to claim 8, further comprising:

a nitrogen supply unit including a nitrogen supplier configured to introduce gaseous nitrogen into the cathode chamber;
an ammonia collection unit including an ammonia collector configured to collect ammonia contained in a discharged product from the cathode chamber; and
an ammonia separation unit including an ammonia separator configured to separate ammonia from the electrolytic solution discharged from the anode chamber.

10. The device according to claim 9, further comprising
an electrolytic solution circulation unit including a circulation pipe configured to circulate the electrolytic solution accommodated in the anode chamber outside the anode chamber, and an electrolytic solution storage tank arranged in the circulation pipe and configured to store the electrolytic solution.

FIG. 1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O_2
21
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13
20
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12
22
23
3
5
6
4
N_2/O_2
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8
9
NH_3
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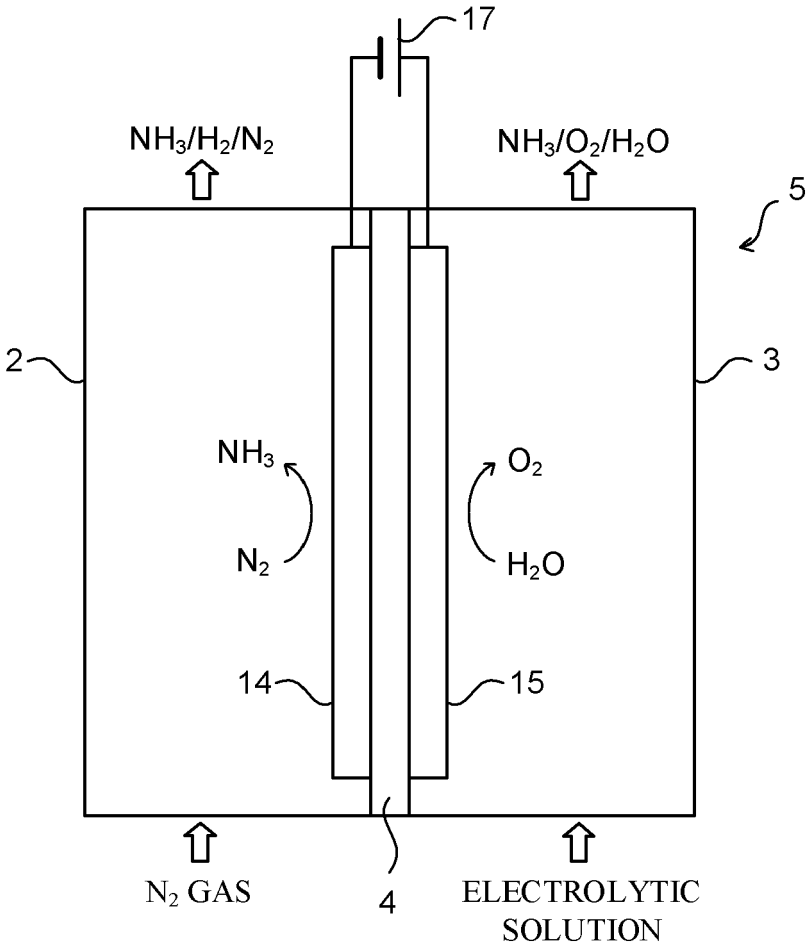
FIG. 2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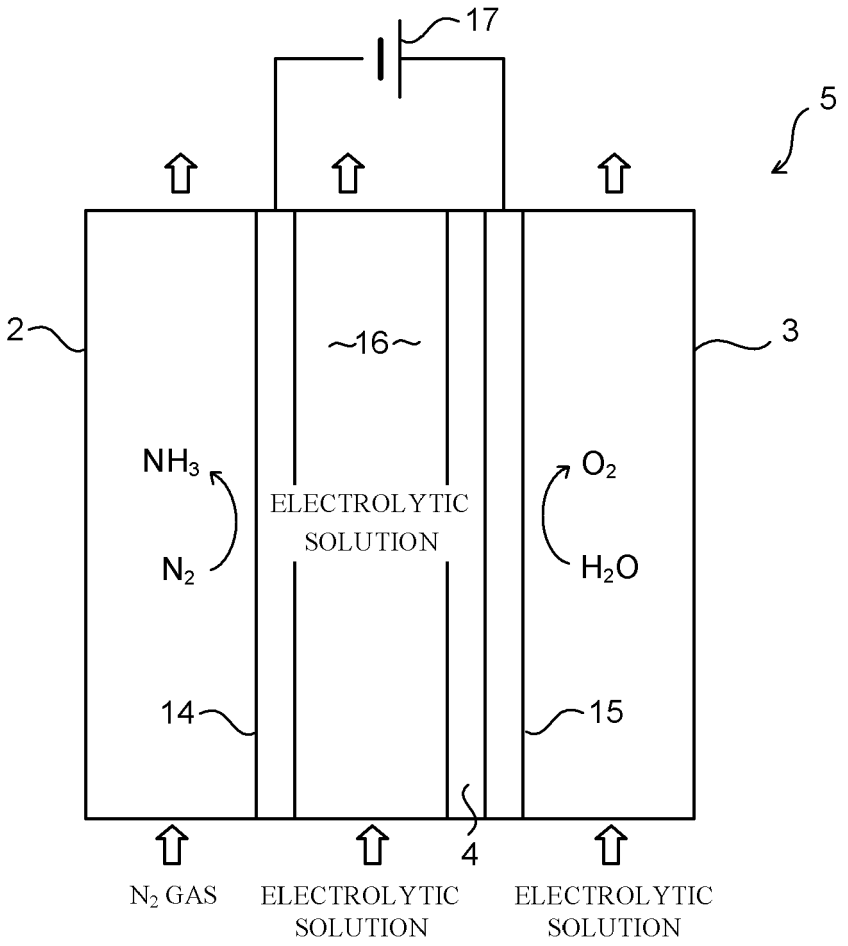
NH3/H2/N2
NH3/O2/H2O
5
2
3
NH3
N2
O2
H2O
14
15
N2 GAS
4
ELECTROLYTIC SOLUTION

FIG. 3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2
16
3
NH3
N2
ELECTROLYTIC SOLUTION
O2
H2O
14
15
4
N2 GAS
ELECTROLYTIC SOLUTION
ELECTROLYTIC SOLUTION