

DESCRIPTION

CONTINUOUS DIRECT SYNTHESIS/RECOVERY METHOD FOR HYDROGEN PEROXIDE USING CATALYST-COATED REACTION TUBE, AND DEVICE THEREFOR

TECHNICAL FIELD

[0001] The present invention relates to a continuous direct synthesis and recovery method for hydrogen peroxide using a catalyst-coated reaction tube, and a device therefor, and more particularly to a direct synthesis method for hydrogen peroxide by which hydrogen peroxide is directly and continuously synthesized from hydrogen and oxygen by using a reaction tube obtained by coating the inner wall of a hollow tube with a noble-metal thin film of a catalyst by electroless plating, or the like, and the directly and continuously synthesized hydrogen peroxide is then continuously recovered as hydrogen peroxide water, and a device therefor. In the present description, the reaction tube obtained by coating the inner wall of a hollow tube with a noble-metal thin film of a catalyst can be referred to as "catalyst-coated reaction tube".

BACKGROUND ART

[0002] Hydrogen peroxide has been widely used, for example, in the fields of water treatment, sterilization, bleaching, and washing, in particular, in the field of semiconductor washing, as an oxidizing agent with a low environmental load that becomes water after reaction with an object to be

treated. Hydrogen peroxide presently circulating in the market is almost entirely synthesized by sequential oxidation-reduction of anthraquinone which is an aromatic organic compound (anthraquinone process). The anthraquinone process involves a multistage reaction and consumes, for example, large amounts of organic reagents and organic solvents. Hence, it has recently been indicated as a source of environmental pollution.

[0003] Meanwhile, a process for directly synthesizing hydrogen peroxide from hydrogen and oxygen is expected to be a simple synthesis process with a low environmental load. Methods for direct synthesis of hydrogen peroxide from hydrogen and oxygen by using various noble metal catalysts have been investigated from a variety of standpoints to achieve such direct synthesis.

[0004] The most important problem associated with the technique for directly synthesizing hydrogen peroxide from hydrogen and oxygen is how to handle safely the so-called detonating gas which is a gaseous mixture of hydrogen and oxygen. Other subjects to be solved associated with industrial implementation of the technique include ensuring the industrial production amount of hydrogen peroxide, increasing concentration thereof, and reducing the amount of the expensive noble metal catalyst to be used in the process. A variety of technological developments and proposals have so far been made to resolve those subjects, and a direct

synthesis method in which a gaseous mixture of hydrogen, oxygen, and nitrogen is continuously supplied into a colloidal dispersion of a metal catalyst, and hydrogen peroxide is accumulated in the immobilized liquid has recently been proposed as the prior art technique (Cited Reference 1).

[0005] With this method, safety of direct synthesis of hydrogen peroxide is ensured by using nitrogen, and the concentration thereof is increased by continuously introducing a gaseous mixture of starting material gases into the immobilized liquid. However, since this is a batch method, and therefore, the following problems are associated therewith, which are, for example, industrial production amounts are difficult to ensure with this method, the metal catalyst colloid should be recovered from the synthesized hydrogen peroxide water, and the generated hydrogen peroxide re-decomposes.

[0006] As another prior art technique, a method by which a liquid (water) and hydrogen, oxygen, and nitrogen gases are supplied at the same time into a solid catalyst packed into a column, and hydrogen peroxide is continuously synthesized by using the solid catalyst packed into the column has been proposed (Cited Reference 2).

[0007] With this method, the liquid flows as a film over the surface of the solid catalyst particles, the gas can form a continuous phase, and the industrial production amount of hydrogen peroxide can be ensured in the continuous process.

However, this method requires an increase in the amount of introduced inactive gas in order to ensure safety. And therefore, the following problems are associated with this method, which are, for example, the amount of hydrogen and oxygen relating to the synthesis is decreased, the synthesized hydrogen peroxide is highly probable to come again into contact with the catalyst and decompose, the amount of catalyst to be used is increased as a result of packing the catalyst into the column, and a load resistance to be caused by mass transfer inside the column is increased.

[0008] And, as another example of prior art, a continuous mode, for example, a continuous synthesis method in which a solid catalyst is packed into a microchannel having a fine flow channel is proposed (Cited Reference 3). With this method, a hydrogen quenching distance is ensured by using the microchannel, and the gas and liquid are supplied at the same time thereto, and thereby, water of the reaction field promotes the extension of the quenching distance and safety thereof is ensured. However, the problems associated with this method are that a load resistance in mass transfer created by packing metal catalyst particles into the microchannel is increased and reactivity in three phases, namely, the catalyst surface, liquid phase, and gas phase, of the reaction field is difficult to control.

[0009] In prior art, as heterogeneous catalysts to be used for the direct synthesis, there are various catalyst species,

for example, single metal particles, alloy particles, and also active carbon or metal oxide supported catalyst and metal complex modified catalyst and the like. Among them, various metal catalysts in which Pd, Pt, Au, PdO, or Pd/C, Pd/Al₂O₃ or the like is supported have been proposed (see, for example, Cited References 4 to 6). However, a problem associated with any of those catalysts is that they have to be used in the form of fine particles or colloid to increase the specific surface area thereof.

[0010] In the above-described methods, a packed type of solid catalyst is used. However, in the direct synthesis of hydrogen peroxide, the use of the packed type of solid catalyst is generally undesirable from the following standpoints that the synthesis catalyst may function also a hydrogen peroxide decomposition catalyst, there is a risk of explosion caused by the continuous gaseous phase including hydrogen and oxygen, and it is necessary to reduce load resistance in mass transfer.

[0011] Patent Reference 1: Japanese Patent Application Publication No. 2007-84372.

Patent Reference 2: Japanese Patent Application Publication No. H06-183703.

Patent Reference 3: International Patent Application Publication No. WO 2010/044271.

Patent Reference 4: Japanese Patent Application Publication No. H05-213607.

Patent Reference 5: Japanese Translation of PCT
Application No. 2004-516921.

Patent Reference 6: Japanese Patent Application
Publication No. S51-4097.

DISCLOSURE OF THE INVENTION

[0012] With the foregoing in view, the inventors have conducted, with consideration for the above-described related art, a comprehensive research aimed at the resolution of the problems inherent to the related art. As the results, by using a reaction tube obtained by coating a noble-metal thin film of a catalyst on the inner wall of a hollow tube by electroless plating, or the like, the inventors have found that smooth mass transfer can be ensured to form a preferable or optimum three-phase interface constituted by a catalyst surface, a liquid phase, and a gas phase. Further, the inventors have also found that a mixed gas of hydrogen and oxygen, which is a detonating gas, can be split by a liquid by forming a slag flow wherein phase states of the gas phase of a gas and the liquid phase of a liquid are caused to be alternately continuous, thereby making it possible to ensure safety of the direct synthesis of hydrogen peroxide, and have repeated subsequent researches to complete the present invention.

[0013] It is an objective of the present invention to provide a manufacturing process which is suitable for clean and safe industrial manufacture of hydrogen peroxide, as an

alternative to the conventional anthraquinone process which consumes a large amount of energy and may cause environmental pollution. Thus, it is an objective of present invention to establish a method for forming an advantageous three-phase interface constituted by a catalyst surface, a liquid phase, and a gas phase, and safely and continuously synthesize hydrogen peroxide from hydrogen and oxygen, thereby providing an industrially suitable method for direct synthesis of hydrogen peroxide which makes it possible to reduce the amount of expensive noble metal catalyst used and perform the operations safely and stably while ensuring the productivity of the target product, and also to provide a device for implementing such a method.

[0014] The present invention is constituted by the following technical features in order to resolve the above-mentioned problems.

(1) A direct synthesis method of hydrogen peroxide from oxygen and hydrogen, comprising:

1) supplying a gas phase of hydrogen and oxygen or air of a starting material gas, and an aqueous phase of a reaction catalyst into a flow channel inside the reaction tube by using a reaction tube having an inner wall of a hollow tube coated with a noble-metal thin film, continuously and directly synthesizing hydrogen peroxide from the hydrogen and the oxygen inside the reaction tube under predetermined reaction temperature and reaction pressure conditions, and continuously

recovering the synthesized hydrogen peroxide as hydrogen peroxide water; and

2) mixing a gas of the starting material gas phase and a liquid of the aqueous phase with a mixer when the hydrogen peroxide synthesized inside the reaction tube is continuously recovered, adjusting a volume flow rate ratio thereof to form a slag flow, in which phase states of the starting material gas phase and the aqueous phase are caused to be alternately continuous, and continuously recovering the synthesized hydrogen peroxide, immediately after synthesized inside the reaction tube, as hydrogen peroxide water by using the slag flow.

(2) The direct synthesis method of hydrogen peroxide according to (1), wherein a reaction tube coated with a thin film constituted by one or more of palladium, an alloy of palladium and gold, a film having gold nanoparticles precipitated on a palladium thin film surface, an alloy of palladium and silver, and a palladium porous film is used as the reaction tube.

(3) The direct synthesis method of hydrogen peroxide according to (1), wherein a reaction tube having a noble-metal thin film coated thereon by electroless plating is used.

(4) The direct synthesis method of hydrogen peroxide according to (1) or (3), wherein a film thickness of the noble-metal thin film is within a range of 0.5 μm to 2 μm .

(5) The direct synthesis method of hydrogen peroxide according to any one of (1) to (4), wherein any of a corrosion-resistant tube selected from a stainless steel tube, an Inconel tube, a Hastelloy tube, and a titanium tube, or a corrosion-resistant double-wall tube selected from a stainless steel tube, an Inconel tube, and a Hastelloy tube provided with a titanium lining on an inner surface is used as the hollow tube.

(6) The direct synthesis method of hydrogen peroxide according to any one of (1) to (4), wherein a fumed silica tube is used as the hollow tube.

(7) The direct synthesis method of hydrogen peroxide according to (5), wherein when a thin film constituted by any one or more of palladium, an alloy of palladium and gold, a film having gold nanoparticles precipitated on a palladium thin film surface, an alloy of palladium and silver, and a palladium porous film is fabricated by electroless plating inside the reaction tube, an oxide coating film of a metal, which serves as a base, is manufactured by high-temperature oxidation at a temperature equal to or higher than 600°C, or by supercritical hydroxylation at a temperature equal to or higher than 374°C.

(8) The direct synthesis method of hydrogen peroxide according to any one of (1) to (7), wherein an inner diameter

of the reaction tube is from 0.05 mm to 10 mm, or from 0.1 mm to 5 mm.

(9) The direct synthesis method of hydrogen peroxide according to any one of (1) to (8), wherein the reaction temperature is within a range of 0°C to 80°C, or within a range of 5°C to 50°C, and the reaction pressure is within a range of 0.1 MPa to 50 MPa, or within a range of 0.1 MPa to 20 MPa.

(10) The direct synthesis method of hydrogen peroxide according to any one of (1) to (9), wherein the hydrogen peroxide synthesized inside the reaction tube is continuously recovered as hydrogen peroxide water in use of water or an acid aqueous solution.

(11) The direct synthesis method of hydrogen peroxide according to (10), wherein the water or acid aqueous solution that recovers hydrogen peroxide synthesized inside the reaction tube includes any one or more ions from a fluoride ion, a chloride ion, a bromide ion, and an iodide ion.

(12) The direct synthesis method of hydrogen peroxide according to (11), wherein the acidic aqueous solution includes any one or more substances from fluorine, chlorine, bromine, and iodine, and a total concentration of the substance in the acidic aqueous solution is within a range of 0.01 mg/L to 100 mg/L.

(13) The direct synthesis method of hydrogen peroxide according to (1), wherein a volume mixing ratio of the gas and

the liquid is 5-50 (gas) : 1 (liquid), and the slag flow is formed by making a volume flow rate ratio of the starting material gas phase and aqueous phase to be recovered of 50 or less of the gas phase per 1 of the aqueous phase, or 10 or less of the gas phase per 1 of the aqueous phase.

(14) The direct synthesis method of hydrogen peroxide according to (1), wherein an inner diameter of an outflow portion of the mixer that mixes the gas of the starting material gas phase and the liquid of the aqueous phase, an inner diameter of the reaction tube, and an inner diameter of a reaction tube joint connecting the reaction tube are the same, and a slag flow size is not changed according to a flow channel.

(15) The direct synthesis method of hydrogen peroxide according to (1), wherein the slag flow is generated by mixing the gas of the starting material gas phase and the liquid of the aqueous phase with a micromixer while controlling a flow rate and a discharge pressure of the starting material gas phase and the aqueous phase, respectively, by using a mass flow controller for the starting material gas phase and a metering pump for the aqueous phase.

(16) The direct synthesis method of hydrogen peroxide according to (1), wherein a stable slag flow is generated by using a T-shaped micromixer as the micromixer.

(17) The direct synthesis method of hydrogen peroxide according to any one of (1) to (12), wherein the volume mixing

ratio of hydrogen and oxygen is hydrogen 10% to 33% and oxygen 90% to 67%, and the ratio (oxygen/hydrogen) of oxygen and hydrogen of the starting material gas phase is equal to or greater than 1.6, or the ratio of oxygen and hydrogen is equal to or greater than 2.0.

(18) The direct synthesis method of hydrogen peroxide according to any one of (10) to (17), wherein the aqueous phase to be recovered from the reaction tube is recirculated to the reaction tube.

(19) A device for direct synthesis of hydrogen peroxide for continuous direct synthesis of hydrogen peroxide from oxygen and hydrogen, comprising:

1) a reaction tube having an inner wall of a hollow tube coated with a noble-metal thin film; a reaction tube joint for connecting the reaction tube; means for supplying a gas phase of hydrogen and oxygen or air of a starting material gas into a flow channel inside the reaction tube; means for supplying an aqueous phase of a reaction catalyst; and means for continuously recovering synthesized hydrogen peroxide, immediately after synthesized inside the reaction tube, in use of water or an acid aqueous solution; and

2) a mixer that forms a slag flow in which phase states of the starting material gas phase and the aqueous phase are caused to be alternately continuous by mixing the gas of the starting material gas phase and the liquid of the aqueous

phase and adjusting a volume flow rate ratio thereof in a flow channel entering the reaction tube, wherein

3) an inner diameter of an outflow portion of the mixer that mixes the gas of the starting material gas phase and the liquid of the aqueous phase, an inner diameter of the reaction tube, and an inner diameter of the reaction tube joint are the same, and a slag flow size is not changed according to a flow channel.

(20) The device for direct synthesis of hydrogen peroxide according to (19), comprising a reaction tube coated with a thin film constituted by any one or more of palladium, an alloy of palladium and gold, an alloy of palladium and silver, and a palladium porous film as the reaction tube having the inner wall of the tube coated with a noble-metal thin film by electroless plating.

(21) The device for direct synthesis of hydrogen peroxide according to (19), wherein a reaction tube coated with the noble-metal thin film by electroless plating is used.

(22) The device for direct synthesis of hydrogen peroxide according to any one of (19) to (21), wherein any of a corrosion-resistant tube selected from a stainless steel tube, an Inconel tube, a Hastelloy tube, and a titanium tube, or a corrosion-resistant double-wall tube selected from a stainless steel tube, an Inconel tube, and a Hastelloy tube provided with a titanium lining on an inner surface is used as the hollow tube.

(23) The device for direct synthesis of hydrogen peroxide according to any one of (19) to (21), wherein a fumed silica tube is used as the hollow tube.

(24) The device for direct synthesis of hydrogen peroxide according to (22), wherein the reaction tube is used, in which when a thin film constituted by any one or more of palladium, an alloy of palladium and gold, a film having gold nanoparticles precipitated on a palladium thin film surface, an alloy of palladium and silver, and a palladium porous film is fabricated by electroless plating inside the reaction tube, an oxide coating film of a metal, which serves as a base, is manufactured by high-temperature oxidation at a temperature equal to or higher than 600°C, or by supercritical hydroxylation at a temperature equal to or higher than 374°C.

(25) The device for direct synthesis of hydrogen peroxide according to any one of (19) to (24), comprising means for continuously recovering the hydrogen peroxide, which has been synthesized inside the reaction tube, as hydrogen peroxide water in use of water or an acid aqueous solution.

(26) The device for direct synthesis of hydrogen peroxide according to any one of (19) to (25), comprising a mass flow controller that controls the supply of the starting material gas phase and a metering pump that controls the supply of the aqueous phase, wherein a micromixer that mixes

the starting material gas phase and the aqueous phase is provided downstream of the mass flow controller and the metering pump, and a slag flow is generated in which phase states of the starting material gas phase and the aqueous phase are caused to be alternately continuous.

(27) The device for direct synthesis of hydrogen peroxide according to any one of (19) to (26), wherein a stable slag flow is generated by using a T-shaped micromixer as the micromixer.

(28) The device for direct synthesis of hydrogen peroxide according to any one of (19) to (26), comprising recirculation means for recirculating the aqueous phase to be recovered from the reaction tube into the reaction tube.

[0015] The present invention will be described hereinbelow in greater detail.

The present invention provides a direct synthesis method of hydrogen peroxide and a device therefor, which comprises, by using a reaction tube obtained by coating an inner wall of a hollow tube with a noble-metal thin film, continuously and directly synthesizing hydrogen peroxide from hydrogen and oxygen inside the reaction tube, and continuously recovering the synthesized hydrogen peroxide as hydrogen peroxide water.

[0016] It is preferred that the reaction tube used in accordance with the present invention is to be constituted by a hollow reaction tube, that is, by a fine hollow tube of a tubular shape, and in the inner space of the fine hollow tube,

the coated surface area of the noble-metal thin film is to be enlarged. In order to increase the surface area to volume ratio, a fine hollow tube with an inner diameter of 0.05 mm to 10 mm is used as the reaction tube. Thus, the inner diameter of the reaction tube is equal to or less than 10 mm, preferably equal to or less than 5 mm. Further, in order to ensure sufficient material diffusion and heat diffusion inside the fine hollow tube, it is desirable that the inner diameter of the reaction tube is to be from 0.1 mm to 1 mm. Furthermore, with consideration for a pressure loss, it is desirable that the inner diameter of the reaction tube is equal to or greater than 0.25 mm.

[0017] The length of the fine hollow tube constituting the reaction tube is an important factor defining the contact time with the noble-metal thin film of the catalyst in the reaction. Therefore, a hydrogen conversion efficiency rises with the increase in the length of the fine hollow tube, but where the tube is too long, the synthesized hydrogen peroxide may be decomposed again. Further, since the pressure loss increases with the length of the fine hollow tube, a preferable or optimal length can be selected according to those factors. More specifically, the length of the fine hollow tube constituting the reaction tube cannot be uniquely determined because the volume changes depending on the inner diameter of the reaction tube to be used, and therefore, the

reaction time (average retention time of gas) differs even when the length is the same.

[0018] Further, since the ratio of the inner surface area (catalyst-coated surface area) to the volume (specific surface area) changes depending on the inner diameter, the reaction results differ depending on the inner diameter even when the volume is the same (the same reaction time), and a preferable or optimum reaction time, that is, the length of the fine hollow tube, can be selected for each inner diameter. When the inner diameter is 1 mm, the reaction time is selected within 2 min, preferably within 1 min.

[0019] A technique of electroless plating that can be realized in a comparatively simple manner by introducing a plating solution into a fine hollow tube can be used for coating the noble-metal thin film of a catalyst on the inner surface of a hollow fine tube constituting the reaction tube. Another advantage of the electroless plating technique is that the thickness of the plated film can be controlled by controlling the concentration and flow-through rate of the plating solution. A merit of the electroless plating method is that a metal thin film can be coated on the surface of not only a metal, but also a nonconductive glass, ceramic, or plastic as a material of the fine hollow tube constituting the reaction tube.

[0020] For example, a metal, alloy, glass, ceramic, plastic, or the like can be preferably used as a material for

the tubular fine hollow tube constituting the reaction tube used in accordance with the present invention. Corrosion-resistance-titanium, nickel alloys, chromium alloys, and iron alloys can be used for the metallic fine hollow tube. In order to improve chemical resistance, the inner surface of the tube may be lined with titanium or a titanium alloy. For example, a corrosion-resistant tube selected from a stainless steel tube, an Inconel tube, a Hastelloy tube, and a titanium tube, or a stainless steel tube, an Inconel tube, a Hastelloy tube, and a fumed silica tube provided with a titanium lining on the inner surface thereof can be preferably used as the abovementioned hollow tube.

[0021] When titanium or a titanium alloy is used for the inner lining, silane coupling treatment is performed as a pretreatment for the electroless plating, and in this case, it is preferred that the titanium surface is to be subjected to oxidation treatment. It is preferred that a strong oxide coating film is to be formed by performing high-temperature oxidation treatment at a temperature equal or higher than 600°C or supercritical hydroxylation treatment at a temperature equal or higher than 374°C as the oxidation treatment of the titanium surface.

[0022] The preferred materials also include silica glass capillaries, which are used in gas chromatography columns, for glass tubes, alumina, titania, and zirconia for ceramic tubes,

and polypropylene, polyethylene, and polyamides for plastic tubes.

[0023] In accordance with the present invention, a reaction tube coated with a thin film constituted by one or more of palladium, an alloy of palladium and gold, a film obtained by precipitating gold nanoparticles on a palladium thin film surface, an alloy of palladium and silver, and a palladium porous film is used as the reaction tube. The coating of the noble-metal thin film of a catalyst on the inner wall of the tubular fine hollow tube constituting the reaction tube is achieved by electroless plating by applying palladium nuclei to the inner wall of the tube and then circulating a plating solution including a complexing agent, a noble metal salt, and a reducing agent inside the fine hollow tube. A solution obtained by dissolving a metal salt such as palladium, silver, platinum, and rhodium, or a metal complex thereof, a complexing agent ensuring stable dissolution thereof, and a reducing agent in an appropriate solvent can be used as the electroless plating solution.

[0024] The film thickness of the noble-metal thin film of the catalyst can be controlled by the amount of the electroless plating solution to be flowed through, and a range of 0.1 μm to 5 μm is preferably selected for the flow-through amount of the electroless plating solution. In order to reduce the amount of the noble metal to be used and ensure a

uniform plated film, a range of 0.5 μm to 2 μm is more preferred for the thickness of the noble-metal thin film of the catalyst.

[0025] In accordance with the present invention, a gas phase of hydrogen and oxygen or air of a starting material gas, and an aqueous phase of a reaction medium are supplied into a flow channel inside the reaction tube, and hydrogen peroxide is continuously and directly synthesized from hydrogen and oxygen inside the reaction tube under predetermined reaction temperature and reaction pressure conditions. In this case, the gas of the starting material gas phase and the liquid of the aqueous phase are mixed with a micromixer, that is, that the mixed gas of hydrogen and oxygen to be mixed with an acidic aqueous solution, while controlling the flow rate and discharge pressure of the starting material gas phase and the aqueous phase, respectively, thereby forming a slag flow in which phase states of the gas phase and liquid phase from the mixer outlet are alternately continuous and recovering continuously the as-synthesized hydrogen peroxide, which has been synthesized inside the reaction tube, as hydrogen peroxide water by using the slag flow. In other words, the slag flow is introduced into the reaction tube coated with a noble-metal thin film of a catalyst, and hydrogen peroxide is continuously recovered in a liquid phase while being synthesized in a gas phase. In order to generate a stable slag flow, it is preferred that, for example, a T-

shaped micromixer is to be used as the micromixer. The gas phase and liquid phase that have exited the reaction tube can be circulated appropriately by returning before the respective mixers. As for the volume mixing ratio of hydrogen and oxygen, the stoichiometric ratio for hydrogen peroxide synthesis is 5 (hydrogen) : 5 (oxygen), but a ratio of hydrogen 10% to 33% and oxygen 90% to 67% is preferred to suppress the reduction caused by hydrogen, which is the side reaction 4 hereinbelow.

[0026] The slag flow is important means for stable and continuous supply of the starting material gas phase and liquid phase, and the flow rate ratio thereof determines the volumes of the gas phase and liquid phase of the slag flow. Therefore, it is preferred that the flow ranges of the gas phase and liquid phase is to be controlled using a mass flow controller and a metering pump, respectively. Further, since the stability of the slag volume is maintained by the constancy of the inner diameter of the flow channel, it is important that the inner diameter of gas phase inlet, inner diameter of liquid phase inlet, inner diameter of mixer outlet, inner diameter of reaction tube, and inner diameter of reaction tube joint do not change and be constant. Where those diameters are fixed, a stable slag volume is maintained.

[0027] In the reaction system of the direct continuous synthesis of hydrogen peroxide in accordance with the present invention, the reaction of reduction with hydrogen, which is

the side reaction 4, becomes vigorous under a condition that the oxygen ratio (oxygen/hydrogen) in the starting material gas demonstrates an excess of hydrogen (equal to or less than 1). Therefore, it is desirable that the condition of the oxygen ratio being equal to or greater than 1.6, preferably equal to or greater than 2.0, be ensured.

[0028] The following reactions 1 to 4 proceed in the direct continuous synthesis of hydrogen peroxide.

1: $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}_2$ (target reaction: synthesis of H_2O_2);

2: $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$ (side reaction: combustion caused by oxidation);

3: $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + 1/2\text{O}_2$ (side reaction: decomposition of H_2O_2);

4: $\text{H}_2\text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}$ (side reaction: reduction with hydrogen).

[0029] The acidic aqueous solution preferably includes one or more of inorganic acids selected from hydrochloric acid, sulfuric acid, and phosphoric acid. For example, a saturated aqueous solution of carbon dioxide including one or more of the inorganic acids can be used. When an inorganic acid is used, the pH of the aqueous solution is 1 to 4, preferably 2 to 3. Further, by adding any one or more substances selected from fluorine, chlorine, bromine, and iodine to the acidic aqueous solution, it is possible to increase the synthesis efficiency of hydrogen peroxide. The total concentration of

those substances in the acidic aqueous solution is preferably within a range of 0.01 mg/L to 100 mg/L.

[0030] The mixer is typically a micromixer, a T-shaped mixer, a static mixer, a swirl mixer, or a multiple lamellar-flow contact-type mixer, and is not particularly limited, but where the objective is to generate stably a slag flow in which the phase states of the gas of the starting material gas phase and the liquid of the aqueous phase are alternately continuous, it is preferred that, for example, a micromixer of a T-shaped mixer or an Y-shaped mixer is to be used. The volume mixing ratio of the gas and the liquid is 100 (gas) : 1 (liquid), preferably 5-50 (gas) : 1 (liquid), and more preferably 5-10 (gas) : 1 (liquid).

[0031] The reaction temperature is preferably within a range of 0°C to 80°C, more preferably within a range of 5°C to 50°C. Since hydrogen peroxide is synthesized from the gases of hydrogen and oxygen, the gas density needs to be increased to increase the concentration of the synthesized hydrogen peroxide. This is one more reason why the reaction under high-temperature conditions is undesirable.

[0032] The reaction pressure is a particularly important factor in terms of increasing the gas density, and in order to increase the concentration of the synthesized hydrogen peroxide, it is preferred that the reaction is to be conducted under high-pressure conditions. However, from the standpoint

of safe industrial application, an ultrahigh pressure needs to be avoided, and it is preferred that the reaction pressure is to be within a range of 0.1 MPa to 50 MPa, in particular, within a range of 0.1 MPa to 20 MPa.

[0033] The reaction time is controlled by the diameter and length of the reaction tube and the sum of the supply flow rates of the gas phase and aqueous solution phase. In this case, a process in which the aqueous solution phase is circulated can be used to reach the target concentration of hydrogen peroxide.

[0034] The reaction tube coated with a noble-metal thin film of a catalyst can be preferably fabricated by a method in which the noble-metal thin film of a catalyst is coated by electroless plating on the inner wall of the reaction tube. A method disclosed in a reference (Japanese Patent No. 4986174) can be used as a method for manufacturing a reaction tube coated by electroless plating with a noble-metal thin film. Palladium-based noble metal alloys such as palladium, an alloy of palladium and gold, a film obtained by precipitating gold nanoparticles on a palladium thin film surface, an alloy of palladium and silver, and a palladium porous film are effective examples of the noble metal for plating. In particular, the conversion ratio of hydrogen can be increased in the presence of gold.

[0035] For example, when the entire surface of a fine hollow tube with an inner diameter of 0.5 mm $\times$ 1000 mm, which

constitutes the reaction tube, is coated with a palladium film with a thickness of 2 μm in the electroless plating method, a total of 37 mg of palladium is used. However, this is a rather small amount when compared with 1 g of active carbon supporting 5% Pd (Pd: 50 mg). Further, reaction tubes obtained by coating, by electroless plating, a noble-metal thin film of a catalyst on hollow fibers arranged side by side in a row can be also used as the reaction tube. In such a case, the reaction tube can be scaled up.

[0036] The device for continuous and direct synthesis of hydrogen peroxide from hydrogen and oxygen is described below. The device for direct synthesis of hydrogen peroxide in accordance with the present invention is characterized by including a reaction tube obtained by coating an inner wall of a hollow tube with a noble-metal thin film, and means for supplying a gas phase of hydrogen and oxygen or air of a starting material gas into the reaction tube, and means for supplying an aqueous phase, and also means for continuously recovering as-synthesized hydrogen peroxide, which has been synthesized inside the reaction tube, with water or an acid aqueous solution.

In the present invention, a reaction tube in which the noble-metal thin film of the reaction tube is coated by electroless plating can be used as the reaction tube.

Further, for example, a device equipped with a reaction tube coated with a thin film constituted by any one or more of

palladium, an alloy of palladium and gold, an alloy of palladium and silver, and a palladium porous film as the reaction tube obtained by coating the inner wall of the tube with a noble-metal thin film can be preferably used as the abovementioned device.

[0037] In the abovementioned device, it is preferred that, for example, any one of a corrosion-resistant tube selected from a stainless steel tube, an Inconel tube, a Hastelloy tube, and a titanium tube, or a corrosion-resistant double-wall tube selected from a stainless steel tube, an Inconel tube, and a Hastelloy tube provided with a titanium lining on the inner surface is to be used as the hollow tube. Further, in the preferred embodiments of the device, a mixer that forms a slag flow in which phase states of the starting material gas phase and the aqueous phase are caused to be alternately continuous is provided in a flow channel entering the reaction tube, and, with regard to the inner diameter, the inner diameter of the outflow portion of the mixer that mixes the gas of the starting material gas phase and the liquid of the aqueous phase, the inner diameter of the reaction tube, and the inner diameter of the reaction tube joint are the same, and in another preferred embodiment, means continuously recovering the hydrogen peroxide synthesized inside the reaction tube as hydrogen peroxide water with water or an acid aqueous solution is provided.

[0038] Further, in the preferred modes for carrying out the invention, the above-mentioned device is provided with a mass flow controller that controls the supply of the starting material gas phase and a metering pump that controls the supply of the aqueous phase, a micromixer that mixes the starting material gas phase and the aqueous phase is provided downstream of the mass flow controller and the metering pump, and a slag flow is generated in which phase states of the starting material gas phase and the aqueous phase are caused to be alternately continuous, and also other preferable modes are a stable slag flow is generated by using a T-shaped micromixer as the micromixer, and recirculation means is provided for recirculating the recover aqueous phase that has exited the reaction tube to the reaction tube.

[0039] A preferred embodiment of the present invention will be explained hereinbelow in greater detail with reference to the appended drawings.

FIG. 1 illustrates the basic concept of hydrogen peroxide synthesis inside a fine hollow tube obtained by coating a noble-metal thin film of a catalyst on the inner wall of the tube and of hydrogen peroxide recovery. The figure shows that the starting material gases (hydrogen and oxygen or air, or hydrogen, oxygen, and an inactive gas) and recover water form a slag flow in which the phase states of the gas and liquid are caused, for example, by a mixer, to be alternately continuous, a hydrogen peroxide synthesis reaction is advanced

by the catalyst of the noble-metal thin film, which is coated on the inner wall of the tube, in the starting material gas portion, and the hydrogen peroxide synthesized herein is immediately thereafter recovered before being decomposed with the recover water portion.

[0040] FIG. 1 is a flowchart of the device for direct synthesis of hydrogen peroxide in which hydrogen peroxide is continuously and directly synthesized from hydrogen and oxygen, this device being an example of the device for implementing the direct synthesis method of hydrogen peroxide in accordance with the present invention.

[0041] The reference numerals in the figure denote the following means. Thus, the reference numerals have the following meaning. B-1: hydrogen gas cylinder; B-2: air gas cylinder; B-3: oxygen gas cylinder; R-1 to R-3: pressure reducing valves; MFC-1 to MFC-3: mass flow controllers; V-1 to V-3: stop valves; CV-1 to CV-5: check valves; SV-1 and SV-2: safety valves; P-1 to P-3: manometers; AT-1: recovery liquid (acid aqueous solution) tank; BV-1: ball valve; LP-1: metering liquid supply pump; M-1: mixer; T-1 and T-2: thermometers; CR-1: catalytic reaction tube; S-1: gas-liquid separator; NV-1: needle valve; BPR-1 and BPR-2: back-pressure valves; MFM-1: mass flowmeter; and G-1: gas collection bag. The means enclosed in the dot line in FIG. 1 are immersed in water in a water tank, and the temperature of water in the water tank is controlled with a thermostatic circulator, thereby controlling

the reaction temperature.

[0042] The device for direct synthesis of hydrogen peroxide and the operation thereof will be described hereinbelow in greater detail.

Hydrogen and oxygen which are starting material gases are supplied from the respective high-pressure gas cylinders (B-1 and B-2), and the flow rate thereof is adjusted to the predetermined level with the mass flow controllers (MFC1 to MFC3) after reducing the pressure to a predetermined level with the pressure reducing valves (R-1 to R-3).

[0043] In this case, the flow rate ratio of hydrogen and oxygen theoretically may be 5 (hydrogen) : 5 (oxygen), and oxygen can be also added in excess. Further, in order to further improve safety, the gas cylinder B-2 can be changed, as necessary, to an inactive gas such as nitrogen and carbon dioxide. The starting material gas mixed at the predetermined flow rate ratio is heated to a predetermined temperature inside the water tank and then introduced into the mixer (M-1).

[0044] Meanwhile, the recover aqueous phase for rapidly recovering the hydrogen peroxide, which has been synthesized inside the reaction tube, into the aqueous phase is supplied from the recovery liquid tank (AT-1) to the suction section of the metering liquid supply pump (LP-1). The recover liquid is heated to a predetermined temperature inside the water tank and then introduced into the mixer (M-1) similarly to the

starting material gas. The recover water used herein may be simple pure water, but the addition of an acid such as sulfuric acid, phosphoric acid, and hydrochloric acid, or the addition of a fluoride ion, chloride ion, bromide ion, and iodide ion can be also performed with the object of increasing the decomposition of the synthesized hydrogen peroxide or the yield and selectivity of the reaction thereof.

[0045] For forming a slag flow in which the phase states of the starting material gas phase and the aqueous phase of the recover water are caused to be alternately continuous, for example, a T-shaped mixer or an Y-shaped mixture is used as the mixer (M-1). In order to form a stable slag flow, the flow rate of the starting material gas is controlled with the mass flow controller to be 10 or fewer times, preferably, 5 or fewer times the recover water amount, and the flow rate of the recover liquid is controlled using the metering pump. The starting material gas and recover liquid are supplied into the catalytic reaction tube (CR-1) in the slag flow state in which the phase states of the gas phase and aqueous phase form alternately continuous flows. The starting material gas is then converted into hydrogen peroxide by the action of the noble metal catalyst coated on the inner wall of the reaction tube, and rapidly recovered with an aqueous phase immediately following the gas phase, thereby forming hydrogen peroxide water which is recovered and stored in the gas-liquid separator (S-1).

[0046] As for the conditions of the synthesis reaction in the device for direct synthesis of hydrogen peroxide, the reaction temperature is preferably set to 0°C to 80°C, more preferably set to 5°C to 50°C. The reaction pressure is preferably set within a range of 0.1 MPa to 50 MPa, more preferably set within a range of 0.1 MPa to 20 MPa. The reaction time depends on the inner diameter of the reaction tube, but where the inner diameter is 1 mm, the reaction time is set within 2 min, preferably within 1 min.

[0047] The inner diameter of the reaction tube used herein is preferably set to 10 mm or less in order to form a stable slag flow. From the standpoint of safety, it is preferred that the inner diameter of the reaction tube is to be set to 1 mm or less which is a hydrogen quenching diameter. For example, palladium, an alloy of palladium and gold, a film obtained by precipitating gold nanoparticles on a palladium thin film surface, an alloy of palladium and silver, and a palladium porous film can be advantageously used as the noble metal catalyst.

[0048] With the object of increasing the concentration of hydrogen peroxide in the recovered liquid, a circulation line (CL-1) can be provided in which a needle valve (NV-1) in the outlet of the gas-liquid separator (S-1) is closed and the recover liquid is returned from the circulation line to the recover liquid tank (AT-1). However, since the noble metal

which is a hydrogen peroxide synthesis catalyst also acts as a decomposition catalyst for the synthesized hydrogen peroxide, this circulation requires attention. Further, a line for recirculating the gas after the reaction can be also provided, and such line can be implemented, as appropriate, with consideration of the reaction gas conversion ratio.

[0049] The following effects can be demonstrated with the present invention.

(1) With the direct synthesis technique of hydrogen peroxide in accordance with the present invention, it is possible to reduce the amount of catalyst to be used which was difficult with the conventional techniques.

(2) Since the reaction tube is used which is coated with a noble-metal thin film of a catalyst by electroless plating, the noble metal surface which is effective as a catalyst can be formed from a micron-order thin film and the amount of the expensive noble metal used can be reduced while fully ensuring the catalyst surface necessary for the reaction.

[0050] (3) By using the device for direct synthesis of hydrogen peroxide which is provided with a reaction field of a tubular shape, it is possible to reduce the load resistance created by mass transfer, eliminate a runaway reaction in the reaction field, and enable a homogeneous synthesis reaction of hydrogen peroxide.

[0051] (4) Safety of direct synthesis of hydrogen peroxide can be ensured with any method selected from a method in which

a mixed gas of hydrogen and oxygen is split by an aqueous solution into a slag flow in which the phase states thereof are alternately continuous, a method in which hydrogen or oxygen is mixed in advance with an aqueous solution, and the mixture is supplied to the reaction field, and a method in which nitrogen or carbon dioxide is supplied at the same time as an inactive gas.

(5) By using a fine hollow tube with an inner diameter of 1 mm or less as the reaction tube, it is possible to realize the concept of the so-called quenching diameter. As a result, the explosion of the gas mixture of hydrogen and oxygen can be suppressed.

[0052] (6) By using the reaction field of a tubular shape in which the load resistance caused by mass transfer is small, it is possible to prevent the synthesized hydrogen peroxide from coming again into contact with the catalyst and decomposing. Further, the reaction in a continuous flow-through mode can greatly increase the productivity of the target product.

[0053] (7) Hydrogen peroxide presently available on the market unavoidably includes organic matter derived from the production method. By contrast, the present invention makes it possible to manufacture and provide ultrahigh-purity hydrogen peroxide for semiconductor applications which require high purity and organic matter-free hydrogen peroxide suitable as a microanalytical reagent.

BRIEF DESCRIPTION OF THE DRAWINGS

[0054] FIG. 1 is a flowchart of the device for direct synthesis of hydrogen peroxide in which hydrogen peroxide is continuously and directly synthesized from hydrogen and oxygen.

FIG. 2 is a visualization flow diagram for verifying the stabilization of the fluidized state of a slag flow.

FIG. 3 depicts the results relating to the density of hydrogen peroxide synthesized in Example 1.

FIG. 4 depicts the results relating to hydrogen conversion ratio, selection ratio of hydrogen peroxide, and yield of hydrogen peroxide during synthesis of hydrogen peroxide in Example 1.

FIG. 5 depicts the results relating to the density of hydrogen peroxide synthesized in Example 2.

FIG. 6 depicts the results relating to hydrogen conversion ratio, selection ratio of hydrogen peroxide, and yield of hydrogen peroxide during synthesis of hydrogen peroxide in Example 1.

FIG. 7 illustrates the connection of a PFA visualization tube for verifying the stabilization of the fluidized state of a slag flow.

BEST MODE FOR CARRYING OUT THE INVENTION

[0055] The present invention will be explained hereinbelow in greater detail on the basis of production examples and

examples thereof, but the present invention is not limited in any way by the below-described production examples and examples.

[0056] Production Example 1

(Formation of palladium nuclei on inner wall of titanium-lined nickel alloy tubular reaction tube)

(1) Manufacture of titanium-lined nickel alloy tubular reaction tube

A titanium-lined nickel alloy tubular reaction tube constituted by a double-wall tube of a fine hollow tube having a hollow portion was manufactured by using a nickel alloy Inconel 625 (trade name) as a material for the outer tube of the double-wall tube constituted by the outer tube and inner tube, using pure titanium as the material for the inner tube, inserting the inner tube made from pure titanium into the outer tube made from the nickel alloy, rolling, and fitting. The same method was applied to a stainless steel tube and a Hastelloy tube provided with a titanium lining on the inner surface.

[0057] (2) Oxidation treatment of titanium surface

Hydrogen peroxide water with a concentration of 0.3 wt% was supplied in the presence of supercritical water under high-temperature and high-pressure conditions (500°C, 30 MPa) from an inlet of the titanium-lined nickel alloy tubular reaction tube constituted by the abovementioned double-wall tube. Oxygen separated from the hydrogen peroxide formed a

homogeneous phase with the supercritical water, thereby generating good oxidizing atmosphere. As a result, the surface of pure titanium of the inner tube was oxidized, a film of titanium oxide was uniformly formed, and a titanium oxide layer with a thickness of about 100 μm was obtained.

[0058] The titanium-lined nickel alloy tubular reaction tube constituted by thus obtained double-wall tube configured of the nickel alloy, pure titanium, and titanium oxide had an inner diameter of 1 mm, an outer diameter of 1.5 mm, a length of 100 cm, and an inner surface area of 31.4 cm^2 .

[0059] (3) Introduction of silane coupling agent

A 1% solution of 3-trimethoxysilylpropyldiethylenetriamine in toluene was introduced as a silane coupling agent for fixing palladium and titanium oxide into the titanium-lined nickel alloy tubular reaction tube constituted by double-wall tube configured of the nickel alloy, pure titanium, and titanium oxide, and the silane coupling agent was retained in a sealed state for 16 h at 70°C.

[0060] (4) Formation of palladium nuclei

Nuclei of palladium particles were attached to the titanium oxide surface as a pretreatment for electroless plating in the titanium-lined nickel alloy tubular reaction tube constituted by thus obtained double-wall tube configured of the nickel alloy, pure titanium, and titanium oxide. More

specifically, 5 ml of 0.1 M aqueous solution of palladium acetate was allowed to flow along the inner wall of the reaction tube, thereby causing adsorption, and then 5 ml of 1 M hydrazine aqueous solution was allowed to flow to precipitate palladium particles as nuclei on the inner wall surface.

[0061] Production Example 2

(Electroless plating of palladium on inner wall of titanium-lined nickel alloy tubular reaction tube)

The titanium-lined nickel alloy tubular reaction tube in the form of a fine hollow tube which was fabricated in the process of Production Example 1 and to which palladium particle nuclei were attached was immersed into a water bath at 60°C, and an aqueous plating solution at 50°C that included 4 mM $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$, 0.15 M EDTA, 1 M ammonia, and 10 mM hydrazine was allowed to flow through as a plating solution at a flow velocity of 0.5 ml per minute from the tip of the fine hollow tube. The supply was stopped once 200 ml of the plating solution was supplied.

[0062] The plating solution flowing out from the end of the tube in this process was sampled, and the amount of palladium contained in the outflowing plating solution was analyzed by ICP emission spectroscopy. As a result, the consumed amount of palladium was 57 mg, and this amount was plated on the surface of the inner wall of the tube. In the outflowing solution, the initial concentration of palladium of 380 ppm

reduced to 10 ppm or less. The SEM observations of the cross section of the tube demonstrated that the thickness of the palladium layer was 3.5 μm .

[0063] Production Example 3

(Electroless plating of palladium and silver on inner wall of titanium-lined nickel alloy tubular reaction tube)

The titanium-lined nickel alloy tubular reaction tube in the form of a fine hollow tube which was fabricated in the process of Production Example 1 and to which palladium particle nuclei were attached was immersed into a water bath at 60°C, and an aqueous plating solution at 60°C that included 9 mM palladium acetate, 1 mM silver nitrate, 0.15 M EDTA, 4 M ammonia, and 10 mM hydrazine was allowed to flow through as a plating solution at a flow velocity of 0.5 ml per minute from the tip of the fine hollow tube.

[0064] The composition of the plating solution in this case was such that the mass ratio of palladium and silver was 90 : 10. After 110 ml of the plating solution was allowed to flow from the tip of the fine hollow tube, the tube was washed with water. The plating solution flowing out from the end of the tube in this process was sampled, and the amount of palladium and silver contained in the outflowing plating solution was analyzed by ICP emission spectroscopy. As a result, the consumed amount of palladium and silver was 67.7 mg and 10.1 mg, respectively, and those amounts were plated on the surface

of the inner wall of the tube. As a mass ratio, those amounts corresponded to 87% and 13%, respectively.

[0065] Production Example 4

(Formation of porous palladium film by selective elution and removal of silver)

A total of 700 ml of 4 M nitric acid was allowed to flow at a temperature of 25°C and a flow velocity of 0.5 ml per minute in the titanium-lined nickel alloy tubular reaction tube in the form of a fine hollow tube which was fabricated in the process of Production Example 3 and was coated with palladium and silver at a ratio of 67.7 mg (87 mass%) : 10.1 mg (13 mass%), silver was selectively eluted and removed, and a porous palladium film was formed. The amounts of eluted palladium and silver were analyzed by ICP emission spectroscopy. The results demonstrated that the remaining amount of palladium was 48.1 mg (94 mass%) and the remaining amount of silver was 2.9 mg (5.7 mass%).

[0066] Production Example 5

The titanium-lined nickel alloy tubular reaction tube in the form of a fine hollow tube which was fabricated in the process of Production Example 3 and was coated with palladium and silver at a ratio of 67.7 mg (87 mass%) : 10.1 mg (13 mass%) was inserted into a quartz tube with an inner diameter of 4 cm and the entire configuration was placed into a tubular furnace. A coating film constituted by a palladium-silver alloy film produced by alloying was formed by heating for 3 h

at 600°C while allowing hydrogen to flow from one end of the fine hollow tube. Prior to heating, X-ray diffraction peaks of palladium ($2\theta = 40.0^\circ$) and silver ($2\theta = 38^\circ$) were observed, but after the heating, a new peak ($2\theta = 39.5^\circ$) of the palladium-silver alloy film was observed.

[0067] Example 1

(Explanation of direct synthesis device)

Direct synthesis of hydrogen peroxide was performed using the direct synthesis device depicted in FIG. 1. The direct synthesis device depicted in FIG. 1 is explained hereinbelow. The device depicted inside the dot line in FIG. 1 is immersed in a water tank to ensure safety and control the reaction temperature. The synthesis temperature of hydrogen peroxide was set to 40°C, and the reaction pressure was controlled using back-pressure valves (BPR-1, BPR-2) at 0.8 MPa with manometers (PT; P-1, P-2, P-3). A liquid circulation line (CL-1) was arranged in the direct synthesis device to enable the circulation of the synthesized hydrogen peroxide.

[0068] A hydrogen cylinder (B-1), an air cylinder (B-2), and optionally an oxygen cylinder (B-3) were used to supply starting material gases to be used for hydrogen peroxide synthesis, and the supply amount of the starting material gases was controlled with a mass flow controllers (MFC; MFC-1, MFC-2, MFC-3) arranged in respective cylinders. As a result, quantitative supply could be performed by setting any desired

composition of the starting material gas. The acid aqueous solution used to recover hydrogen peroxide was an aqueous solution including sulfuric acid at 0.02 mol/L and sodium bromide at 26 ppm. This acid aqueous solution was loaded in advance into an acid aqueous solution tank (Acid tank; AT-1) and quantitatively supplied with a pump (LP-1).

[0069] (Direct synthesis of hydrogen peroxide from hydrogen, oxygen, and air: 1)

The direct synthesis device depicted in FIG. 1 was used and the concentration of hydrogen in the starting materials gas to be used for synthesis of hydrogen peroxide was set to 21.4 vol%. The concentration of oxygen was changed to 1, 1.6, and 2.0 as an oxygen ratio (oxygen/hydrogen) by using air and oxygen. The starting material gas included 30 vol% or more of nitrogen, which is an inactive gas, under any of the abovementioned conditions.

[0070] In the synthesis and recovery of hydrogen peroxide, the total supply rate of the starting material gas was 7 ml/min (0.8 MPa, 40°C) and the supply rate of acid aqueous solution (sulfuric acid at 0.02 mol/L with the addition of 20 ppm of bromine) was 1 ml/min. The starting material gas and acid aqueous solution were mixed with a 1/8-inch T-shaped mixer before being introduced into the reaction tube of the direct synthesis device. The starting material gas and acid aqueous solution were supplied into the reaction tube in the form of a slag flow, in which the phase states of the gas

phase of the gas and the aqueous phase of the liquid were caused to be alternately continuous, and flowed out from the reaction tube after continuous synthesis and recovery. The gas and acid aqueous solution remaining after the reaction were separated with a gas-liquid separator (S-1). The synthesized hydrogen peroxide was collected together with the acid aqueous solution inside the gas-liquid separator (Separator; S-1), and the remaining gas was collected in a gas bag (G-1) through the back-pressure valve (BPR-1) and mass flowmeter (MFM: MFM-1).

[0071] The direct synthesis device depicted in FIG. 1 used a reaction tube coated by electroless plating with a single layer of palladium as a synthesis catalyst. The reaction time was 64 sec. The reaction tube had a length of $2\text{ m} \times 5 = 10\text{ m}$, and the outer diameter of the reaction tube was 1/8 inch, similarly to the T-shaped mixer for gas-liquid mixing. The inner diameter of the union of the reaction tube joint for connecting the reaction tube was the same as the inner diameter of the reaction tube to prevent the phase state of the slag flow from distortion caused by changes in the inner diameter.

[0072] After the acid aqueous solution collected in the gas-liquid separator (S-1) was recovered, the concentration of the synthesized hydrogen peroxide was quantitatively determined by a iodine coulometric titration method (Hydrogen Peroxide Counter HP-300, manufactured by Hiranuma Sangyo Co.,

Ltd.). The remaining gas collected in the gas back (G-1) was analyzed by TCD gas chromatography (GC-8A, manufactured by Shimazu Corp.), and a hydrogen conversion ratio was determined.

[0073] As a result, the concentration of the synthesized hydrogen peroxide was 10940 ppm under the condition of hydrogen concentration of 21.4 vol% and oxygen concentration of 42.9 vol%. The hydrogen conversion ratio under such conditions was 95.7%, the hydrogen peroxide selection ratio was 63.6%, and the hydrogen peroxide yield, which was determined by the formula: $\text{Yield} = (\text{Hydrogen conversion ratio}) \times (\text{Hydrogen peroxide selection ratio}) / 100$, was 60.9%.

[0074] Example 2

(Direct synthesis of hydrogen peroxide from hydrogen, oxygen, and air: 2)

The synthesis of hydrogen peroxide was conducted by using the direct synthesis device depicted in FIG. 1 under the same conditions as in Example 1, except that the concentration of hydrogen was 13.6 vol% and the oxygen ratio was changed from 0.5 to 4.0 in the starting material gas composition.

[0075] The concentration of the synthesized hydrogen peroxide increased with the increase in oxygen concentration in the starting material gas, and when the oxygen ratio (oxygen/hydrogen) in the starting material was less than 2, the selection ratio of hydrogen peroxide dropped rapidly with the decrease in oxygen ratio. When the oxygen ratio was equal

to or greater than 2, the selection ratio of hydrogen peroxide slightly increased with the increase in oxygen ratio.

[0076] Example 3

(Increase in concentration of hydrogen peroxide due to circulation of synthesized hydrogen peroxide water)

The synthesis (one cycle) of hydrogen peroxide was conducted by using the direct synthesis device depicted in FIG. 1 under the same conditions as in Example 1, except that the concentration of hydrogen was 13.6 vol% and the concentration of air was 86.4% (oxygen/hydrogen = 1.3) in the starting material gas composition. Then, the synthesized hydrogen peroxide thus obtained was recovered and charged into the acid aqueous solution tank (AT-1), and the synthesis (two cycles) of hydrogen peroxide was performed, under the same conditions as in the first cycle, by the method of circulating the synthesized hydrogen peroxide in which only the acidic aqueous solution was changed to the synthesized hydrogen peroxide water obtained in the first cycle.

[0077] The concentration of hydrogen peroxide was 4903 ppm in the one cycle and 7710 ppm in the two cycles. This result has confirmed that the concentration of the synthesized hydrogen peroxide can be increased by circulating only the synthesized hydrogen peroxide water.

[0078] Example 4

(Stabilization of fluidized state of slag flow)

An experiment with a visualization flow depicted in FIG. 2 was conducted by using a PFA visualization tube (PFA tube) to verify the stabilization of the fluidized state of the slag flow in which the phase states of the gas phase and aqueous phase were caused to be alternately continuous.

A 1/8-inch T-shaped mixer (M-2) was used as the gas-liquid mixer (Mixer) for mixing the starting material gas and water, and the 1/8-inch PFA visualization tube (PFA Tube, inner diameter 1.6 mm) was connected to the mixer outlet. The tubes of two types were prepared, namely, a tube with a total length of 10 m in which the 1/8-inch PFA visualization tube was joined with a straight union (Union; U-1, inner diameter 2.3 mm) of the reaction tube joint at a 2-m interval, and a 10-m tube that did not use the straight union.

[0079] A gas-liquid separator (Separator; S-2) was connected to the outlet of the PFA visualization tube, only the gas was discharged to the outside of the system through the back-pressure valve (BPR; BPR-3), and the liquid was accumulated in the gas-liquid separator. Initially, the pressure inside the entire device was raised with air (Ar), and the pressure inside the entire device was maintained at 0.8 MPa with the back-pressure valve (BPR-3) while allowing the air flow therethrough. Water colored by the addition of red food colorant to facilitate visualization was supplied at 1 ml/min, the air supply rate was changed as 1.2 ml/min, 2 ml/min, 6 ml/min, and 12 ml/min, and the fluidized state of

the slag flow was observed and confirmed in the tube joined by the straight union and the seamless tube having no union.

[0080] In either of the abovementioned tube joined by the straight union and the seamless tube having no union, a stable slag flow was discharged into the PFA visualization tube, but after the flow passed through the union where the inner diameter of the piping changed, the air and liquid coalesced and homogeneous segments collapsed. Meanwhile, in the tube having no unions, the size of the segment in the inlet was maintained till the outlet at a distance of 10 m from the inlet. This result indicates that the inner diameter of the piping needs to be the same in order to maintain the continuity of the fluidized state of the slag flow.

INDUSTRIAL APPLICABILITY

[0081] As described in detail hereinabove, the present invention relates to a continuous direct synthesis and recovery method for hydrogen peroxide using a catalyst-coated reaction tube, and a device therefor. As a result of using the reaction tube coated with a noble-metal thin film of a catalyst, it is possible to form a noble metal surface effective as a catalyst from a micron-order thin film and reduce the amount used of the expensive noble metal while fully ensuring the catalyst surface necessary for the reaction. With the device for continuous direct synthesis of hydrogen peroxide in accordance with the present invention, as

a result of using the reaction field of a tubular shape, it is possible to reduce the load resistance created by mass transfer, eliminate a runaway reaction in the reaction field, and enable a homogeneous synthesis reaction. In accordance with the present invention, safety of direct synthesis of hydrogen peroxide can be ensured with any method selected from a method in which a mixed gas of hydrogen and oxygen is split by an aqueous solution into a slag flow in which the mixed gas and the aqueous solution are alternately continuous, a method in which hydrogen or oxygen is mixed in advance with an aqueous solution, and the mixture is supplied to the reaction field, and a method in which nitrogen or carbon dioxide is supplied at the same time as an inactive gas. The present invention is useful in providing a new method for directly and continuously synthesizing hydrogen peroxide from hydrogen and oxygen by using a catalyst-coated reaction tube obtained by coating the inner wall of a hollow tube with a noble-metal thin film of a catalyst, and then continuously recovering the synthesized hydrogen peroxide with an aqueous phase as hydrogen peroxide water, and also providing a device for implementing the method.

EXPLANATION OF REFERENCE NUMERALS

[0082] B: gas cylinder (B-1: hydrogen; B-2: air; B-3: oxygen; B-4: nitrogen);

R: cylinder regulator;

MFC: mass flow controller (MFC-1, MFC-2, MFC-3, MFC-4);

V: valve (V-1, V-2, V-3, V-4);

CV: check valve (CV-1, CV-2, CV-3, CV-4, CV-5, CV-6, CV-7);

PT: manometer (P-1, P-2, P-3, P-4);

SV: safety valve (SV-1, SV-2);

AT-1: Acid tank; acid aqueous solution tank;

BV-1: ball valve;

LP: liquid pump (LP-1, LP-2);

TI: thermometer (T-1, T-2);

CR-1: Catalytic reactor; palladium catalyst reaction tube;

S: gas-liquid separator (Separator; S-1, S-2);

NV: needle valve (NV-1);

BPR: back-pressure valve (BPR-1, BPR-2, BPR-3);

MFM: mass flowmeter (MFM-1);

G-1: gas bag;

M: T-shaped mixer (Mixer; M-1, M2);

WT-1: water tank (Water tank);

Union: straight unit (U-1);

CL-1: circulation line.

CLAIMS

1. A direct synthesis method of hydrogen peroxide from oxygen and hydrogen, comprising:

1) supplying a gas phase of hydrogen and oxygen or air of a starting material gas, and an aqueous phase of a reaction catalyst into a flow channel inside the reaction tube by using a reaction tube having an inner wall of a hollow tube coated with a noble-metal thin film, continuously and directly synthesizing hydrogen peroxide from the hydrogen and the oxygen inside the reaction tube under predetermined reaction temperature and reaction pressure conditions, and continuously recovering the synthesized hydrogen peroxide as hydrogen peroxide water; and

2) mixing a gas of the starting material gas phase and a liquid of the aqueous phase with a mixer when the hydrogen peroxide synthesized inside the reaction tube is continuously recovered, adjusting a volume flow rate ratio

thereof to form a slag flow, in which phase states of the starting material gas phase and the aqueous phase are caused to be alternately continuous, and continuously recovering the synthesized hydrogen peroxide, immediately after synthesized inside the reaction tube, as hydrogen peroxide water by using the slag flow.

2. The direct synthesis method of hydrogen peroxide according to claim 1, wherein a reaction tube coated with a thin film constituted by one or more of palladium, an alloy of palladium and gold, a film having gold nanoparticles precipitated on a palladium thin film surface, an alloy of palladium and silver, and a palladium porous film is used as the reaction tube.

3. The direct synthesis method of hydrogen peroxide according to claim 1, wherein a reaction tube having a

noble-metal thin film coated thereon by electroless plating is used.

4. The direct synthesis method of hydrogen peroxide according to claim 1 or 3, wherein a film thickness of the noble-metal thin film is within a range of 0.5 μm to 2 μm .

5. The direct synthesis method of hydrogen peroxide according to any one of claims 1 to 4, wherein any of a corrosion-resistant tube selected from a stainless steel tube, an Inconel tube, a Hastelloy tube, and a titanium tube, or a corrosion-resistant double-wall tube selected from a stainless steel tube, an Inconel tube, and a Hastelloy tube provided with a titanium lining on an inner surface is used as the hollow tube.

6. The direct synthesis method of hydrogen peroxide according to any one of claims 1 to 4, wherein a fumed silica tube is used as the hollow tube.

7. The direct synthesis method of hydrogen peroxide according to claim 5, wherein when a thin film constituted by any one or more of palladium, an alloy of palladium and gold, a film having gold nanoparticles precipitated on a palladium thin film surface, an alloy of palladium and silver, and a palladium porous film is fabricated by electroless plating inside the reaction tube, an oxide coating film of a metal, which serves as a base, is manufactured by high-temperature oxidation at a temperature equal to or higher than 600°C, or by supercritical hydroxylation at a temperature equal to or higher than 374°C.

8. The direct synthesis method of hydrogen peroxide according to any one of claims 1 to 7, wherein an inner diameter of the reaction tube is from 0.05 mm to 10 mm, or from 0.1 mm to 5 mm.

9. The direct synthesis method of hydrogen peroxide according to any one of claims 1 to 8, wherein the reaction temperature is within a range of 0°C to 80°C, or within a range of 5°C to 50°C, and the reaction pressure is within a range of 0.1 MPa to 50 MPa, or within a range of 0.1 MPa to 20 MPa.

10. The direct synthesis method of hydrogen peroxide according to any one of claims 1 to 9, wherein the hydrogen peroxide synthesized inside the reaction tube is continuously recovered as hydrogen peroxide water in use of water or an acid aqueous solution.

11. The direct synthesis method of hydrogen peroxide according to claim 10, wherein the water or acid aqueous solution that recovers hydrogen peroxide synthesized inside the reaction tube includes any one or more ions from a fluoride ion, a chloride ion, a bromide ion, and an iodide ion.

12. The direct synthesis method of hydrogen peroxide according to claim 11, wherein the acidic aqueous solution includes any one or more substances from fluorine, chlorine, bromine, and iodine, and a total concentration of the substance in the acidic aqueous solution is within a range of 0.01 mg/L to 100 mg/L.

13. The direct synthesis method of hydrogen peroxide according to claim 1, wherein a volume mixing ratio of the gas and the liquid is 5-50 (gas) : 1 (liquid), and the slag flow is formed by making a volume flow rate ratio of the

starting material gas phase and aqueous phase to be recovered of 50 or less of the gas phase per 1 of the aqueous phase, or 10 or less of the gas phase per 1 of the aqueous phase.

14. The direct synthesis method of hydrogen peroxide according to claim 1, wherein an inner diameter of an outflow portion of the mixer that mixes the gas of the starting material gas phase and the liquid of the aqueous phase, an inner diameter of the reaction tube, and an inner diameter of a reaction tube joint connecting the reaction tube are the same, and a slag flow size is not changed according to a flow channel.

15. The direct synthesis method of hydrogen peroxide according to claim 1, wherein the slag flow is generated by mixing the gas of the starting material gas phase and the liquid of the aqueous phase with a micromixer while

controlling a flow rate and a discharge pressure of the starting material gas phase and the aqueous phase, respectively, by using a mass flow controller for the starting material gas phase and a metering pump for the aqueous phase.

16. The direct synthesis method of hydrogen peroxide according to claim 1, wherein a stable slag flow is generated by using a T-shaped micromixer as the micromixer.

17. The direct synthesis method of hydrogen peroxide according to any one of claims 1 to 12, wherein the volume mixing ratio of hydrogen and oxygen is hydrogen 10% to 33% and oxygen 90% to 67%, and the ratio (oxygen/hydrogen) of oxygen and hydrogen of the starting material gas phase is equal to or greater than 1.6, or the ratio of oxygen and hydrogen is equal to or greater than 2.0.

18. The direct synthesis method of hydrogen peroxide according to any one of claims 10 to 17, wherein the aqueous phase to be recovered from the reaction tube is recirculated to the reaction tube.

19. A device for direct synthesis of hydrogen peroxide for continuous direct synthesis of hydrogen peroxide from oxygen and hydrogen, comprising:

1) a reaction tube having an inner wall of a hollow tube coated with a noble-metal thin film; a reaction tube joint for connecting the reaction tube; means for supplying a gas phase of hydrogen and oxygen or air of a starting material gas into a flow channel inside the reaction tube; means for supplying an aqueous phase of a reaction catalyst; and means for continuously recovering synthesized hydrogen peroxide, immediately after synthesized inside the reaction tube, in use of water or an acid aqueous solution; and

2) a mixer that forms a slag flow in which phase states of the starting material gas phase and the aqueous phase are caused to be alternately continuous by mixing the gas of the starting material gas phase and the liquid of the aqueous phase and adjusting a volume flow rate ratio thereof in a flow channel entering the reaction tube, wherein

3) an inner diameter of an outflow portion of the mixer that mixes the gas of the starting material gas phase and the liquid of the aqueous phase, an inner diameter of the reaction tube, and an inner diameter of the reaction tube joint are the same, and a slag flow size is not changed according to a flow channel.

20. The device for direct synthesis of hydrogen peroxide according to claim 19, comprising a reaction tube coated with a thin film constituted by any one or more of palladium, an alloy of palladium and gold, an alloy of palladium and silver, and a palladium porous film as the

reaction tube having the inner wall of the tube coated with a noble-metal thin film by electroless plating.

21. The device for direct synthesis of hydrogen peroxide according to claim 19, wherein a reaction tube coated with the noble-metal thin film by electroless plating is used.

22. The device for direct synthesis of hydrogen peroxide according to any one of claims 19 to 21, wherein any of a corrosion-resistant tube selected from a stainless steel tube, an Inconel tube, a Hastelloy tube, and a titanium tube, or a corrosion-resistant double-wall tube selected from a stainless steel tube, an Inconel tube, and a Hastelloy tube provided with a titanium lining on an inner surface is used as the hollow tube.

23. The device for direct synthesis of hydrogen peroxide according to any one of claims 19 to 21, wherein a fumed silica tube is used as the hollow tube.

24. The device for direct synthesis of hydrogen peroxide according to claim 22, wherein the reaction tube is used, in which when a thin film constituted by any one or more of palladium, an alloy of palladium and gold, a film having gold nanoparticles precipitated on a palladium thin film surface, an alloy of palladium and silver, and a palladium porous film is fabricated by electroless plating inside the reaction tube, an oxide coating film of a metal, which serves as a base, is manufactured by high-temperature oxidation at a temperature equal to or higher than 600°C, or by supercritical hydroxylation at a temperature equal to or higher than 374°C.

25. The device for direct synthesis of hydrogen peroxide according to any one of claims 19 to 24, comprising means for continuously recovering the hydrogen peroxide, which has been synthesized inside the reaction tube, as hydrogen peroxide water in use of water or an acid aqueous solution.

26. The device for direct synthesis of hydrogen peroxide according to any one of claims 19 to 25, comprising a mass flow controller that controls the supply of the starting material gas phase and a metering pump that controls the supply of the aqueous phase, wherein a micromixer that mixes the starting material gas phase and the aqueous phase is provided downstream of the mass flow controller and the metering pump, and a slag flow is generated in which phase states of the starting material gas phase and the aqueous phase are caused to be alternately continuous.

27. The device for direct synthesis of hydrogen peroxide according to any one of claims 19 to 26, wherein a stable slug flow is generated by using a T-shaped micromixer as the micromixer.

28. The device for direct synthesis of hydrogen peroxide according to any one of claims 19 to 26, comprising recirculation means for recirculating the aqueous phase to be recovered from the reaction tube into the reaction tube.