

DESCRIPTION

ANION EXCHANGER, MIXTURE OF ANION EXCHANGER AND CATION
EXCHANGER, MIXED BED COMPRISING ANION EXCHANGER AND CATION
5 EXCHANGER, PRODUCTION PROCESSES THEREFOR, AND METHOD FOR
PURIFYING AQUEOUS HYDROGEN PEROXIDE SOLUTION

TECHNICAL FIELD

[0001]

10 The present invention relates to an anion exchanger, a mixture that includes an
anion exchanger and a cation exchanger (anion exchanger-cation exchanger mixture), a
mixed bed that includes an anion exchanger and a cation exchanger (anion
exchanger-cation exchanger mixed bed), methods for producing the same, and a method
for purifying a hydrogen peroxide solution.

15

BACKGROUND ART

[0002]

A hydrogen peroxide solution is used in a wide variety of fields (i.e., a
paper/pulp bleaching agent, an industrial oxidizing agent, waste water treatment, and a
20 cleaning agent used for a semiconductor production process). In the field of a wet
cleaning process that is performed during a semiconductor production process, a large
amount of hydrogen peroxide solution is used for an ammonia-hydrogen peroxide
solution (RCA:SC-1) cleaning process that removes particulate contamination, a
hydrochloric acid-hydrogen peroxide solution (RCA:SC-2) cleaning process that ionizes
25 and removes metal contamination, and the like.

[0003]

An increase in purity is desired for ultrapure water and reagents used to remove

such contamination, and a high-quality hydrogen peroxide solution in which the content of impurities is reduced as much as possible is desired. In particular, the yield of semiconductor devices decreases when a metal component such as iron, aluminum, sodium, calcium, or magnesium is included in a hydrogen peroxide solution or the like.

5 [0004]

A method that utilizes an ion-exchange resin and a method that utilizes reverse osmosis membrane have been proposed as a method for reducing the impurity content in a hydrogen peroxide solution. When an anion-exchange resin (ion-exchange resin) is used in the OH form, the decomposition reaction of hydrogen peroxide may proceed, and the generation of heat or the production of oxygen gas may occur (i.e., it may be difficult to implement safe operation). Therefore, the anion-exchange resin is used after effecting conversion into a carbonate form or a bicarbonate form.

[0005]

Patent Literature 1 discloses that a high-purity hydrogen peroxide solution that has a metal concentration of 0.1 ppb or less and a total organic carbon concentration of 10 ppm or less can be obtained by sequentially utilizing a mixed bed ion-exchange resin, an adsorbent device, and a mixed bed ion-exchange resin.

[0006]

Patent Literature 2 discloses that a hydrogen peroxide solution can be purified to have high purity by sequentially bringing a hydrogen peroxide solution into contact with an H^+ -form cation-exchange resin, an F^- -form ion-exchange resin, a CO_3^{2-} -form or HCO_3^- -form anion-exchange resin, and an H^+ -form cation-exchange resin. .

[0007]

Patent Literature 3 discloses that a high-purity hydrogen peroxide solution can be obtained by sequentially bringing an ion-exchange resin into contact with a high-purity mineral acid aqueous solution having a metal component concentration of 0.1 ppb by weight or less, and ultrapure water having a metal component concentration

of 0.1 ppb by weight or less.

[0008]

Patent Literature 4 discloses a method that brings a crude hydrogen peroxide solution into contact with an anion-exchange resin that is converted into a carbonate form using ammonium carbonate, or an anion-exchange resin that is converted into a bicarbonate form using ammonium bicarbonate.

[0009]

Patent Literature 5 discloses a method for producing a purified hydrogen peroxide solution that utilizes a reverse osmosis membrane formed of a polyamide-based or polyvinyl alcohol-based composite membrane.

CITATION LIST

PATENT LITERATURE

[0010]

Patent Literature 1: Japanese Patent No. 3715371

Patent Literature 2: Japanese Patent No. 4056695

Patent Literature 3: Japanese Patent No. 3171058

Patent Literature 4: Japanese Patent No. 3608211

Patent Literature 5: JP-A-2011-68533

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0011]

In Patent Literature 1 to 3, a carbonate or hydrogen carbonate aqueous solution is normally used to convert the anion-exchange resin into a bicarbonate form. However, when using a mixture that includes an anion-exchange resin and a cation-exchange resin, or a mixed bed that includes an anion-exchange resin and a cation-exchange resin, a carbonate or hydrogen carbonate aqueous solution cannot be

used to convert the anion-exchange resin into a bicarbonate form since the cation of the cation-exchange resin is exchanged with the cation of carbonate or hydrogen carbonate. [0012]

In Patent Literature 4, ammonium carbonate or ammonium bicarbonate is used
5 to convert the anion-exchange resin into a carbonate form or a bicarbonate form.
However, when using a mixture that includes an anion-exchange resin and a cation-exchange resin, or a mixed bed that includes an anion-exchange resin and a cation-exchange resin, the cation of the cation-exchange resin is exchanged with an ammonium ion. Moreover, since only the anion-exchange resin is packed in a resin
10 column, converted into a carbonate form or a bicarbonate form, and then mixed with the cation-exchange resin, workability deteriorates, and contamination with impurities may occur.

[0013]

In Patent Literature 1 to 3, a carbonate or hydrogen carbonate aqueous solution
15 having a salt concentration as high as 5 to 15 wt% is normally used to convert the anion-exchange resin into a carbonate form or a bicarbonate form. Therefore, since the aqueous solution having a high salt concentration is brought into contact with the ion exchanger after removing impurities from a hydrogen peroxide solution, sodium ions and the like are eluted from the resin when the resin is brought into contact with a
20 hydrogen peroxide solution even if the resin is regenerated and sufficiently washed with water. Moreover, it is necessary to use a large amount of purified water or ultrapure water for washing the resin.

[0014]

Patent Literature 5 discloses a method that utilizes a reverse osmosis membrane.
25 In this case, however, there is a problem in which the membrane may deteriorate due to the contact with a high-concentration hydrogen peroxide solution, and the blocking rate may decrease.

[0015]

In Patent Literature 4, ammonium carbonate or ammonium bicarbonate is used to solve the above problem. However, a definite metal (impurity) standard value is not specified for ammonium carbonate or ammonium bicarbonate, and the concentration
5 specified by some standard values may be high, even if there is a definite metal standard in a part of metal species. Moreover, it is necessary to dispose of liquid waste.

[0016]

Various types of functional water other than a hydrogen peroxide solution are also purified using an anion-exchange resin. Since an anion-exchange resin can be
10 used for various applications, there is a potential demand for a novel anion exchanger, and a mixture or a mixed bed that includes a novel anion exchanger and a cation exchanger.

[0017]

An object of the invention is to provide a method for producing an anion
15 exchanger-cation exchanger mixture and a method for producing an anion exchanger-cation exchanger mixed bed that can convert the anion exchanger included in the mixture that includes the anion exchanger and the cation exchanger, or the anion exchanger included in the mixed bed that includes the anion exchanger and the cation exchanger, into an anion exchanger that includes a bicarbonate form, or includes a
20 bicarbonate form and a carbonate form, in a state of the mixture or the mixed bed.

Another object of the invention is to provide an anion exchanger that exhibits an excellent capability to purify a hydrogen peroxide solution, water, an aqueous solution, or an organic solvent that is purified using an anion exchanger, a mixture or a mixed bed that includes the anion exchanger and a cation exchanger, and methods for producing
25 the same.

Another object of the invention is to provide a method for efficiently purifying a hydrogen peroxide solution.

SOLUTION TO PROBLEM

[0018]

Several aspects of the invention solve the above problems as described below.

- (1) An anion exchanger-cation exchanger mixture including a mixture that includes
5 an anion exchanger (A) and a cation exchanger, wherein the anion exchanger (A) is an anion exchanger that includes a bicarbonate form (-HCO_3), or an anion exchanger that includes a bicarbonate form (-HCO_3) and a carbonate form (-CO_3).
- (2) An anion exchanger-cation exchanger mixture obtained by performing an anion exchanger conversion step (1) that brings a carbon dioxide aqueous solution obtained by
10 dissolving carbon dioxide in purified water or ultrapure water into contact with a mixture that includes an anion exchanger (B) and a cation exchanger to convert the anion exchanger (B) into an anion exchanger (A) that includes a bicarbonate form, or includes a bicarbonate form and a carbonate form, to obtain a mixture that includes the anion exchanger (A) and the cation exchanger.
- 15 (3) The anion exchanger-cation exchanger mixture according to (1) or (2), wherein the anion exchanger (A) is an anion exchanger in which the ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form is 70 eq% or more.
- (4) An anion exchanger-cation exchanger mixed bed including a mixed bed that is
20 packed in an ion exchange column and includes an anion exchanger (A) and a cation exchanger, wherein the anion exchanger (A) is an anion exchanger that includes a bicarbonate form (-HCO_3), or an anion exchanger that includes a bicarbonate form (-HCO_3) and a carbonate form (-CO_3).
- (5) The anion exchanger-cation exchanger mixed bed according to (4), wherein the
25 anion exchanger (A) is an anion exchanger in which the ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form is 70 eq% or more.

- (6) A method for producing an anion exchanger-cation exchanger mixture including an anion exchanger conversion step (1) that brings a carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water into contact with a mixture that includes an anion exchanger (B) and a cation exchanger to convert the anion exchanger (B) into an anion exchanger (A) that includes a bicarbonate form, or includes a bicarbonate form and a carbonate form, to obtain a mixture that includes the anion exchanger (A) and the cation exchanger.
- (7) The method for producing an anion exchanger-cation exchanger mixture according to (6), wherein the anion exchanger (A) is an anion exchanger in which the ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form is 70 eq% or more.
- (8) The method for producing an anion exchanger-cation exchanger mixture according to (6) or (7), wherein the anion exchanger conversion step (1) brings the carbon dioxide aqueous solution into contact with the mixture that includes the anion exchanger (B) and the cation exchanger until the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the mixture that includes the anion exchanger (B) and the cation exchanger to the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the mixture that includes the anion exchanger (B) and the cation exchanger $((\text{electrical conductivity after contact} / \text{electrical conductivity before contact}) \times 100))$ reaches 90% or more.
- (9) A method for producing an anion exchanger-cation exchanger mixed bed including an anion exchanger conversion step (2) that brings a carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water into contact with a mixed bed that is packed in an ion exchange column and includes an anion exchanger (B) and a cation exchanger to convert the anion exchanger (B) into an anion exchanger (A) that includes a bicarbonate form, or includes a bicarbonate form

and a carbonate form, to obtain a mixed bed that includes the anion exchanger (A) and the cation exchanger.

(10) The method for producing an anion exchanger-cation exchanger mixed bed according to (9), wherein the anion exchanger (A) is an anion exchanger in which the ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form is 70 eq% or more.

(11) The method for producing an anion exchanger-cation exchanger mixed bed according to (9) or (10), wherein the anion exchanger conversion step (2) supplies the carbon dioxide aqueous solution to the ion exchange column until the ratio of the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column to the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column ((electrical conductivity at outlet / electrical conductivity at inlet) $\times$ 100)) reaches 90% or more.

(12) A method for purifying a hydrogen peroxide solution including:

an anion exchanger conversion step (2) that brings a carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water into contact with a mixed bed that is packed in an ion exchange column and includes an anion exchanger (B) and a cation exchanger to convert the anion exchanger (B) into an anion exchanger (A) that includes a bicarbonate form, or includes a bicarbonate form and a carbonate form, to obtain a mixed bed that includes the anion exchanger (A) and the cation exchanger; and

a hydrogen peroxide solution purification step that supplies a crude hydrogen peroxide solution to the ion exchange column so that the crude hydrogen peroxide solution is brought into contact with the mixed bed that includes the anion exchanger (A) and the cation exchanger to obtain a purified hydrogen peroxide solution.

(13) The method for purifying a hydrogen peroxide solution according to (12), wherein the anion exchanger conversion step (2) supplies the carbon dioxide aqueous

- solution to the ion exchange column until the ratio of the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column to the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column ((electrical conductivity at outlet / electrical conductivity at inlet) × 100)) reaches 90% or more.
- (14) An anion exchanger including a bicarbonate form (-HCO_3), or including a bicarbonate form (-HCO_3) and a carbonate form (-CO_3).
- (15) An anion exchanger obtained by bringing a carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water into contact with an OH-form anion exchanger.
- (16) The anion exchanger according to (14) or (15), wherein the ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form is 70 eq% or more.
- (17) A method for producing an anion exchanger including an anion exchanger conversion step (3) that brings a carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water into contact with an anion exchanger (B) to convert the anion exchanger (B) into an anion exchanger (A) that includes a bicarbonate form, or includes a bicarbonate form and a carbonate form.
- (18) The method for producing an anion exchanger according to (17), wherein the anion exchanger (A) is an anion exchanger in which the ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form is 70 eq% or more.
- (19) The method for producing an anion exchanger according to (17) or (18), wherein the anion exchanger conversion step (3) brings the carbon dioxide aqueous solution into contact with the anion exchanger (B) until the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger (B) to the electrical conductivity of the carbon dioxide aqueous solution

before being brought into contact with the anion exchanger (B) ((electrical conductivity after contact / electrical conductivity before contact) $\times$ 100)) reaches 90% or more.

(20) A method for purifying a hydrogen peroxide solution including:

an anion exchanger conversion step (4) that brings a carbon dioxide aqueous
5 solution obtained by dissolving carbon dioxide in purified water or ultrapure water into contact with an anion exchanger (B) that is packed in an ion exchange column to convert the anion exchanger (B) into an anion exchanger (A) that includes a bicarbonate form, or includes a bicarbonate form and a carbonate form; and

a hydrogen peroxide solution purification step that supplies a crude hydrogen
10 peroxide solution to the ion exchange column so that the crude hydrogen peroxide solution is brought into contact with the anion exchanger (A) to obtain a purified hydrogen peroxide solution.

(21) The method for purifying a hydrogen peroxide solution according to (20),
wherein the anion exchanger conversion step (4) and the hydrogen peroxide solution
15 purification step are repeated alternately.

(22) The method for purifying a hydrogen peroxide solution according to (20) or (21),
wherein the anion exchanger conversion step (4) supplies the carbon dioxide aqueous solution to the ion exchange column until the ratio of the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column to the
20 electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column ((electrical conductivity at outlet / electrical conductivity at inlet) $\times$ 100)) reaches 90% or more.

ADVANTAGEOUS EFFECTS OF INVENTION

[0019]

25 The aspects of the invention thus provide a method for producing an anion exchanger-cation exchanger mixture and a method for producing an anion exchanger-cation exchanger mixed bed that can convert the anion exchanger included in

the mixture that includes the anion exchanger and the cation exchanger, or the anion exchanger included in the mixed bed that includes the anion exchanger and the cation exchanger, into an anion exchanger that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form, in a state of the mixture or the mixed bed.

5 The aspects of the invention thus provide an anion exchanger that exhibits an excellent capability to purify a hydrogen peroxide solution, water, an aqueous solution, or an organic solvent that is purified using an anion exchanger, a mixture or a mixed bed that includes the anion exchanger and a cation exchanger, and methods for producing the same.

10 The aspects of the invention thus provide a method for efficiently purifying a hydrogen peroxide solution.

BRIEF DESCRIPTION OF DRAWINGS

[0020]

15 FIG. 1 is a flow diagram (examples).

FIG. 2 is a graph illustrating a change in the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column and the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column (examples).

20 FIG. 3 is a graph illustrating a change in acetic acid removal with the passing of time (Example and Comparative Example).

DESCRIPTION OF EMBODIMENTS

[0021]

25 An anion exchanger-cation exchanger mixture according to one embodiment of the invention includes a mixture that includes an anion exchanger (A) and a cation exchanger, wherein the anion exchanger (A) is an anion exchanger that includes a

bicarbonate form (-HCO_3), or an anion exchanger that includes a bicarbonate form (-HCO_3) and a carbonate form (-CO_3).

[0022]

An anion exchanger-cation exchanger mixed bed according to one embodiment
5 of the invention includes a mixed bed that is packed in an ion exchange column and includes an anion exchanger (A) and a cation exchanger, wherein the anion exchanger (A) is an anion exchanger that includes a bicarbonate form (-HCO_3), or an anion exchanger that includes a bicarbonate form (-HCO_3) and a carbonate form (-CO_3).

[0023]

10 The anion exchanger (A) used in connection with the anion exchanger-cation exchanger mixture according to one embodiment of the invention and the anion exchanger-cation exchanger mixed bed according to one embodiment of the invention is an anion exchanger that includes a bicarbonate form (-HCO_3), or an anion exchanger that includes a bicarbonate form (-HCO_3) and a carbonate form (-CO_3) (i.e., an anion
15 exchanger that includes an anion-exchange group of which the counter anion is a bicarbonate ion (-HCO_3 ion), or an anion exchanger that includes an anion-exchange group of which the counter anion is a bicarbonate ion (-HCO_3 ion), and an anion-exchange group of which the counter anion is a carbonate ion (-CO_3 ion)). The anion exchanger (A) is an anion exchanger that includes a resin as a base, and includes
20 an anion-exchange group that is introduced into the resin. The anion exchanger (A) is a styrene-based gel-type or MR-type anion-exchange resin or organic porous anion exchanger. With regard to the expressions “bicarbonate form (R-HCO_3)” and “carbonate form (R-CO_3)” used herein, the carbonate form is present in the form of R-HCO_3^- , and the bicarbonate form is present in the form of R-CO_3^{2-} under actual usage
25 conditions.

[0024]

The anion exchanger (A) used in connection with the anion exchanger-cation

exchanger mixture according to one embodiment of the invention and the anion
exchanger-cation exchanger mixed bed according to one embodiment of the invention is
characterized in that the ratio of the exchange capacity of the bicarbonate form to the
total exchange capacity of the bicarbonate form and the carbonate form ($((\text{number of}$
5 $\text{equivalents of bicarbonate-form anion-exchange group} / (\text{number of equivalents of}$
 $\text{bicarbonate-form anion-exchange group} + \text{number of equivalents of carbonate-form}$
 $\text{anion-exchange group})) \times 100$) is preferably 70 eq% or more, more preferably 75 eq%
or more, and particularly preferably 80 eq% or more. When the ratio of the exchange
capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form
10 and the carbonate form is within the above range, it is possible to obtain a high
capability to purify a hydrogen peroxide solution, water, an aqueous solution, or an
organic solvent that is purified using an anion exchanger.

[0025]

The anion exchanger (A) used in connection with the anion exchanger-cation
15 exchanger mixture according to one embodiment of the invention and the anion
exchanger-cation exchanger mixed bed according to one embodiment of the invention
may further have an ionic form other than the bicarbonate form and the carbonate form
as long as purification is not adversely affected. It is preferable that the ratio of the
total exchange capacity of the bicarbonate form and the carbonate form to the total
20 exchange capacity of the anion exchanger ($((\text{number of equivalents of bicarbonate-form}$
 $\text{anion-exchange group} + \text{number of equivalents of carbonate-form anion-exchange}$
 $\text{group}) / \text{total number of equivalents of anion-exchange group}) \times 100$) be 50 eq% or
more, more preferably 60 eq% or more, still more preferably 70 eq% or more, still more
preferably 80 eq% or more, still more preferably 95 eq% or more, still more preferably
25 99 eq% or more, and still more preferably 100 eq%. When the ratio of the total
exchange capacity of the bicarbonate form and the carbonate form to the total exchange
capacity of the anion exchanger is within the above range, it is possible to obtain a high

capability to purify a hydrogen peroxide solution, water, an aqueous solution, or an organic solvent that is purified using an anion exchanger.

[0026]

When the anion exchanger (A) used in connection with the anion
5 exchanger-cation exchanger mixture according to one embodiment of the invention and the anion exchanger-cation exchanger mixed bed according to one embodiment of the invention further has an ionic form other than the bicarbonate form and the carbonate form, the ionic form other than the bicarbonate form and the carbonate form may be a Cl form, an OH form, or the like. Note that the decomposition reaction of hydrogen
10 peroxide may easily proceed when purifying a hydrogen peroxide solution if the content of OH form in the anion exchanger (A) is too high. Therefore, when the anion exchanger (A) is used to purify hydrogen peroxide, the ratio of the exchange capacity of the OH form to the total exchange capacity of the anion exchanger (A) is preferably 1 eq% or less, more preferably 0.1 eq% or less, and particularly preferably 0 eq%.

15 [0027]

A styrene-divinylbenzene copolymer is preferable as the resin (into which the anion-exchange group is introduced) that is included in the anion exchanger (A) used in connection with the anion exchanger-cation exchanger mixture according to one
embodiment of the invention and the anion exchanger-cation exchanger mixed bed
20 according to one embodiment of the invention.

[0028]

Examples of the anion exchanger (A) used in connection with the anion
exchanger-cation exchanger mixture according to one embodiment of the invention and the anion exchanger-cation exchanger mixed bed according to one embodiment of the
25 invention include a strongly basic type I anion exchanger that includes a quaternary ammonium group as a functional group, wherein only an alkyl group is bonded to the nitrogen atom of the ammonium group; a strongly basic type II anion exchanger that

includes a quaternary ammonium group as a functional group, wherein an alkyl group and an alkanol group are bonded to the nitrogen atom of the ammonium group; and a weakly basic anion exchanger that includes a primary to tertiary amino group as a functional group. Among these, the strongly basic type I anion exchanger is preferable.

[0029]

When the anion exchanger (A) used in connection with the anion exchanger-cation exchanger mixture according to one embodiment of the invention and the anion exchanger-cation exchanger mixed bed according to one embodiment of the invention is a particulate anion-exchange resin, the average particle size of the anion-exchange resin is preferably 0.2 to 1.0 mm, and particularly preferably 0.4 to 0.8 mm. When the anion exchanger (A) used in connection with the anion exchanger-cation exchanger mixture according to one embodiment of the invention and the anion exchanger-cation exchanger mixed bed according to one embodiment of the invention is an organic porous anion exchanger, the organic porous anion exchanger has a structure in which a number of cell-like macropores overlap each other, and communicating holes formed by the macropores that overlap each other are formed in the skeleton formed of a resin (i.e., continuous macropore structure).

[0030]

The cation exchanger used in connection with the anion exchanger-cation exchanger mixture according to one embodiment of the invention and the anion exchanger-cation exchanger mixed bed according to one embodiment of the invention is a cation exchanger that includes a resin as a base, and includes a cation-exchange group that is introduced into the resin. The cation exchanger is a styrene-based gel-type or MR-type cation-exchange resin or organic porous ion exchanger. A styrene-divinylbenzene copolymer is preferable as the resin (into which the cation-exchange group is introduced) included in the cation-exchanger.

[0031]

Examples of the cation-exchange group (that is introduced into the resin) included in the cation exchanger used in connection with the anion exchanger-cation exchanger mixture according to one embodiment of the invention and the anion
5 exchanger-cation exchanger mixed bed according to one embodiment of the invention include a sulfonic acid group.

[0032]

When the cation exchanger used in connection with the anion exchanger-cation exchanger mixture according to one embodiment of the invention and the anion
10 exchanger-cation exchanger mixed bed according to one embodiment of the invention is a particulate cation-exchange resin, the average particle size of the cation-exchange resin is preferably 0.2 to 1.0 mm, and particularly preferably 0.4 to 0.8 mm. When the cation exchanger used in connection with the anion exchanger-cation exchanger mixture according to one embodiment of the invention and the anion exchanger-cation
15 exchanger mixed bed according to one embodiment of the invention is an organic porous cation exchanger, the organic porous cation exchanger has a structure in which a number of cell-like macropores overlap each other, and communicating holes formed by the macropores that overlap each other are formed in the skeleton formed of a resin (i.e., continuous macropore structure).

20 [0033]

The mixture that includes the anion exchanger (A) and the cation exchanger (i.e., the anion exchanger-cation exchanger mixture according to one embodiment of the invention) includes a particulate anion-exchange resin (A) and a particulate cation-exchange resin in a mixed state.

25 [0034]

The mixed bed that includes the anion exchanger (A) and the cation exchanger (i.e., the anion exchanger-cation exchanger mixed bed according to one embodiment of

the invention) may be (i) a bed that is formed by a mixture that includes a particulate anion-exchange resin (A) and a particulate cation-exchange resin (i.e., mixed bed), or (ii) a bed that includes a layer that is formed by the anion exchanger (A) (e.g., particulate anion-exchange resin (A) or organic porous anion exchanger (A)), and a layer that is formed by the cation exchanger (e.g., particulate cation-exchange resin or organic porous cation exchanger) (i.e., dual-layer bed that includes the layer formed by the anion exchanger (A) and the layer formed by the cation exchanger).

[0035]

A method for producing an anion exchanger-cation exchanger mixture according to one embodiment of the invention includes an anion exchanger conversion step (1) that brings a carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water into contact with a mixture that includes an anion exchanger (B) and a cation exchanger to convert the anion exchanger (B) into an anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form, to obtain a mixture that includes the anion exchanger (A) and the cation exchanger.

[0036]

A method for producing an anion exchanger-cation exchanger mixed bed according to one embodiment of the invention includes an anion exchanger conversion step (2) that brings a carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water into contact with a mixed bed that is packed in an ion exchange column and includes an anion exchanger (B) and a cation exchanger to convert the anion exchanger (B) into an anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form, to obtain a mixed bed that includes the anion exchanger (A) and the cation exchanger.

[0037]

The method for producing an anion exchanger-cation exchanger mixture

according to one embodiment of the invention and the method for producing an anion exchanger-cation exchanger mixed bed according to one embodiment of the invention differ from each other in that the method for producing an anion exchanger-cation exchanger mixture brings the carbon dioxide aqueous solution into contact with the mixture that includes the anion exchanger (B) and the cation exchanger, and the method for producing an anion exchanger-cation exchanger mixed bed brings the carbon dioxide aqueous solution into contact with the mixed bed that is packed in an ion exchange column and includes the anion exchanger (B) and the cation exchanger. Note that the method for producing an anion exchanger-cation exchanger mixture according to one embodiment of the invention and the method for producing an anion exchanger-cation exchanger mixed bed according to one embodiment of the invention are identical to each other in that the carbon dioxide aqueous solution is brought into contact with the anion exchanger (B) in the presence of the cation exchanger to convert the anion exchanger (B) into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form.

[0038]

The anion exchanger conversion step (1) brings the carbon dioxide aqueous solution into contact with the mixture that includes the anion exchanger (B) and the cation exchanger to convert the anion exchanger (B) included in the mixture into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form. The anion exchanger conversion step (2) brings the carbon dioxide aqueous solution into contact with the mixed bed that is packed in an ion exchange column and includes the anion exchanger (B) and the cation exchanger to convert the anion exchanger (B) included in the mixed bed into the anion exchanger (A). Note that the mixture that includes the anion exchanger (B) and the cation exchanger includes a particulate anion-exchange resin (B) and a particulate cation-exchange resin in a mixed state. The mixed bed that includes the anion exchanger (B) and the cation

exchanger may be (i) a bed that is formed by a mixture that includes a particulate anion-exchange resin (B) and a particulate cation-exchange resin (i.e., mixed bed), or (ii) a bed that includes a layer that is formed by the anion exchanger (B) (e.g., particulate anion-exchange resin (B) or organic porous anion exchanger (B)), and a layer that is formed by the cation exchanger (e.g., particulate cation-exchange resin or organic porous cation exchanger) (i.e., dual-layer bed that includes the layer formed by the anion exchanger (B) and the layer formed by the cation exchanger).

[0039]

The anion exchanger (B) used in connection with the anion exchanger conversion step (1) and the anion exchanger conversion step (2) is an anion exchanger that is converted into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form. When a crude hydrogen peroxide solution is purified using an OH-form anion exchanger (i.e., an anion exchanger in which the counter anion of the anion-exchange group is an OH ion) (i.e., strongly basic anion exchanger), hydrogen peroxide is decomposed when hydrogen peroxide is brought into contact with the OH-form anion exchanger. When a crude hydrogen peroxide solution is purified using a Cl-form anion exchanger (i.e., an anion exchanger in which the counter anion of the anion-exchange group is a Cl ion), the Cl ions flow out into the treatment solution due to an ion-exchange reaction with the target ions (i.e., it is impossible to effect purification). Therefore, the method for producing an anion exchanger-cation exchanger mixture according to one embodiment of the invention and the method for producing an anion exchanger-cation exchanger mixed bed according to one embodiment of the invention convert the anion exchanger into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form.

[0040]

The anion exchanger conversion step (1) brings the carbon dioxide aqueous

solution into contact with the mixture that includes an OH-form anion exchanger, a Cl-form anion exchanger, or the like (i.e., an anion exchanger (anion exchanger (B)) that is converted into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form) and the cation exchanger to

5 convert the anion exchanger (B) included in the mixture into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form. When the treatment target water (i.e., a hydrogen peroxide solution, water, or an aqueous solution that is purified using a mixture that includes an anion exchanger and a cation exchanger) is continuously purified using the mixture that includes the anion

10 exchanger (A) (that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form) and the cation exchanger, the bicarbonate ions included in the anion exchanger (A) included in the mixture are exchanged with impurity anions included in the treatment target water. Therefore, when the treatment target water has been continuously purified for a certain time, it is necessary to regenerate the anion

15 exchanger that has been subjected to the ion-exchange reaction with impurity anions into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form. The anion exchanger (B) (that is converted into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form) that is subjected to the anion exchanger

20 conversion step (1) that is performed to obtain the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form, includes the anion exchanger that is converted into the anion exchanger (A), and the anion exchanger that has been subjected to the ion-exchange reaction with impurity anions included in the treatment target water during the purification of the treatment target water (e.g.,

25 hydrogen peroxide solution), and is subjected again to the anion exchanger conversion step (1).

[0041]

The anion exchanger conversion step (2) brings the carbon dioxide aqueous solution into contact with the mixed bed that is packed in an ion exchange column and includes an OH-form anion exchanger, a Cl-form anion exchanger, or the like (i.e., an anion exchanger (anion exchanger (B)) that is converted into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form) and the cation exchanger to convert the anion exchanger (B) included in the mixed bed into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form. When the treatment target water (i.e., a hydrogen peroxide solution, water, or an aqueous solution that is purified using a mixed bed that includes an anion exchanger and a cation exchanger) is continuously purified using the mixed bed that includes the anion exchanger (A) (that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form) and the cation exchanger, the bicarbonate ions included in the anion exchanger (A) included in the mixed bed are exchanged with impurity anions included in the treatment target water. Therefore, when the treatment target water has been continuously purified for a certain time, it is necessary to regenerate the anion exchanger that has been subjected to the ion-exchange reaction with impurity anions into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form. The anion exchanger (B) (that is converted into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form) that is subjected to the anion exchanger conversion step (2) that is performed to obtain the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form, includes the anion exchanger that is converted into the anion exchanger (A), and the anion exchanger that has been subjected to the ion-exchange reaction with impurity anions included in the treatment target water during the purification of the treatment target water (e.g., hydrogen peroxide solution), and is subjected again to the anion exchanger conversion step (2).

[0042]

The anion exchanger (A) obtained by the anion exchanger conversion step (1) and the anion exchanger conversion step (2) is an anion exchanger that includes a bicarbonate form (-HCO_3), or an anion exchanger that includes a bicarbonate form (-HCO_3) and a carbonate form (-CO_3). The ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion exchanger (A) is not particularly limited, but is preferably 50 eq% or more, more preferably 60 eq% or more, still more preferably 70 eq% or more, still more preferably 80 eq% or more, still more preferably 95 eq% or more, still more preferably 99 eq% or more, and still more preferably 100 eq%. The ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form is preferably 70 eq% or more, more preferably 75 eq% or more, and particularly preferably 80 eq% or more.

[0043]

The anion exchanger (B) that is subjected to the anion exchanger conversion step (1) and the anion exchanger conversion step (2) is an anion exchanger that includes a resin as a base, and includes an anion-exchange group that is introduced into the resin. The anion exchanger (B) is a styrene-based gel-type or MR-type anion-exchange resin or organic porous anion exchanger. A styrene-divinylbenzene copolymer is preferable as the resin (into which the anion-exchange group is introduced) included in the anion exchanger (B).

[0044]

Examples of the anion exchanger (B) that is subjected to the anion exchanger conversion step (1) and the anion exchanger conversion step (2) include a strongly basic type I anion exchanger that includes a quaternary ammonium group as a functional group, wherein only an alkyl group is bonded to the nitrogen atom of the ammonium group; a strongly basic type II anion exchanger that includes a quaternary ammonium

group as a functional group, wherein an alkyl group and an alkanol group are bonded to the nitrogen atom of the ammonium group; and a weakly basic anion exchanger that includes a primary to tertiary amino group as a functional group. Among these, the strongly basic type I anion exchanger is preferable. An OH-form anion exchanger is
5 preferable as the anion exchanger (B) that is subjected to the anion exchanger conversion step (1) and the anion exchanger conversion step (2).

[0045]

When the anion exchanger (B) that is subjected to the anion exchanger conversion step (1) and the anion exchanger conversion step (2) is a particulate
10 anion-exchange resin, the average particle size of the anion-exchange resin is preferably 0.2 to 1.0 mm, and particularly preferably 0.4 to 0.8 mm. When the anion exchanger (B) that is subjected to the anion exchanger conversion step (1) and the anion exchanger conversion step (2) is an organic porous anion exchanger, the organic porous anion exchanger has a structure in which a number of cell-like macropores overlap each other,
15 and communicating holes formed by the macropores that overlap each other are formed in the skeleton formed of a resin (i.e., continuous macropore structure).

[0046]

The cation exchanger that is subjected to the anion exchanger conversion step (1) and the anion exchanger conversion step (2) is a cation exchanger that includes a
20 resin as a base, and includes a cation-exchange group that is introduced into the resin. The cation exchanger is a styrene-based gel-type or MR-type cation-exchanger. A styrene-divinylbenzene copolymer is preferable as the resin (into which the cation-exchange group is introduced) included in the cation-exchanger.

[0047]

25 Examples of the cation-exchange group (that is introduced into the resin) included in the cation exchanger that is subjected to the anion exchanger conversion step (1) and the anion exchanger conversion step (2) include a sulfonic acid group.

[0048]

When the cation exchanger that is subjected to the anion exchanger conversion step (1) and the anion exchanger conversion step (2) is a particulate cation-exchange resin, the average particle size of the cation-exchange resin is preferably 0.2 to 1.0 mm, and particularly preferably 0.4 to 0.8 mm. When the cation exchanger that is subjected to the anion exchanger conversion step (1) and the anion exchanger conversion step (2) is an organic porous cation exchanger, the organic porous cation exchanger has a structure in which a number of cell-like macropores overlap each other, and communicating holes formed by the macropores that overlap each other are formed in the skeleton formed of a resin (i.e., continuous macropore structure).

[0049]

The carbon dioxide aqueous solution that is used in connection with the anion exchanger conversion step (1) and the anion exchanger conversion step (2) is obtained by dissolving carbon dioxide in purified water or ultrapure water. The purified water or the ultrapure water is obtained by treating raw water using a water purifier or an ultrapure water system that removes ions and a non-ionic substance from raw water. It is preferable to use purified water having a resistivity of $1.0 \text{ M}\Omega \cdot \text{cm}$ or more, more preferably ultrapure water having a resistivity of $10 \text{ M}\Omega \cdot \text{cm}$ or more, and particularly preferably ultrapure water having a resistivity of $18 \text{ M}\Omega \cdot \text{cm}$ or more.

[0050]

The carbon dioxide concentration in the carbon dioxide aqueous solution that is used in connection with the anion exchanger conversion step (1) and the anion exchanger conversion step (2) is not particularly limited (as long as carbon dioxide is dissolved in purified water or ultrapure water), but is preferably 1 to 2,000 mg/L, and particularly preferably 20 to 2,000 mg/L. It is possible to reduce the treatment time and the amount of water used by increasing the carbon dioxide concentration in the carbon dioxide aqueous solution.

[0051]

The carbon dioxide aqueous solution may be prepared (i.e., carbon dioxide may be dissolved in purified water or ultrapure water) using an arbitrary method. For example, the carbon dioxide aqueous solution may be prepared using a method for
5 producing functional water that is used for washing electronic parts. For example, the carbon dioxide aqueous solution may be prepared using a method that dissolves carbon dioxide using a hollow fiber membrane, a method that bubbles carbon dioxide directly into a pipe, a method that injects carbon dioxide, and dissolves the carbon dioxide using a dispersion means such as a static mixer, a method that supplies carbon dioxide to a gas
10 dissolution tank on the upstream side of a pump that supplies ultrapure water, and dissolves the carbon dioxide by stirring inside the pump, or the like. It is preferable to dissolve carbon dioxide using a hollow fiber membrane in order to efficiently dissolve carbon dioxide up to the saturation concentration. When using a gas cylinder in order to supply carbon dioxide, it is preferable to provide a particulate removal filter that
15 removes microparticles having a particle size of 0.5 μm or less in a gas supply pipe. It is particularly preferable to provide a particulate removal filter that removes microparticles having a particle size of 0.2 μm or less.

[0052]

When preparing the carbon dioxide aqueous solution, the supply amount of
20 carbon dioxide that is dissolved in purified water or ultrapure water is controlled using a gas mass flow controller. The carbon dioxide concentration is continuously monitored using a conductivity meter.

[0053]

The temperature at which the carbon dioxide aqueous solution is brought into
25 contact with the mixture that includes the anion exchanger (B) and the cation exchanger or the mixed bed that includes the anion exchanger (B) and the cation exchanger in the anion exchanger conversion step (1) or the anion exchanger conversion step (2) is

preferably set to be as low as possible in order to increase the solubility of carbon dioxide, but is preferably 5 to 40°C, and particular preferably 10 to 30°C, from the viewpoint of energy consumption. When the carbon dioxide aqueous solution is passed through the ion exchange column that is packed with the mixed bed that includes the anion exchanger (B) and the cation exchanger in the anion exchanger conversion step (2), the carbon dioxide aqueous solution may be supplied to the ion exchange column by a single-pass operation. Note that a recycle tank and a recycle pump may be provided in the subsequent stage of the ion exchange column, and the used water may be recycled as raw water for preparing the carbon dioxide aqueous solution in order to reduce the amount of purified water or ultrapure water to be used. When recycling water, the amount of carbon dioxide to be supplied can be reduced by feeding back the value measured by a conductivity meter, and controlling the amount of carbon dioxide to be supplied.

[0054]

In the anion exchanger conversion step (1), some or all of the counter anions included in the anion exchanger (B) that is included in the mixture that includes the anion exchanger (B) and the cation exchanger are converted into a bicarbonate ion (-HCO_3) or a carbonate ion (-CO_3) to obtain the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form. In the anion exchanger conversion step (2), some or all of the counter anions included in the anion exchanger (B) that is included in the mixed bed that includes the anion exchanger (B) and the cation exchanger are converted into a bicarbonate ion (-HCO_3) or a carbonate ion (-CO_3) to obtain the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form.

[0055]

The anion exchanger (A) that is obtained by the anion exchanger conversion step (1) and the anion exchanger conversion step (2) is an anion exchanger that includes a

bicarbonate form (-HCO_3), or an anion exchanger that includes a bicarbonate form (-HCO_3) and a carbonate form (-CO_3) (i.e., an anion exchanger that includes an anion-exchange group of which the counter anion is a bicarbonate ion (-HCO_3 ion), or an anion exchanger that includes an anion-exchange group of which the counter anion is a bicarbonate ion (-HCO_3 ion), and an anion-exchange group of which the counter anion is a carbonate ion (-CO_3 ion)). With regard to the expressions “bicarbonate form (R-HCO_3)” and “carbonate form (R-CO_3)” used herein, the carbonate form is present in the form of R-HCO_3^- , and the bicarbonate form is present in the form of R-CO_3^{2-} under actual usage conditions.

10 [0056]

The ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion exchanger (A) (that is obtained by the anion exchanger conversion step (1) and the anion exchanger conversion step (2)) is not particularly limited, but is preferably 50 eq% or more, more preferably 60 eq% or more, still more preferably 70 eq% or more, still more preferably 80 eq% or more, still more preferably 95 eq% or more, still more preferably 99 eq% or more, and still more preferably 100 eq%. Specifically, the anion exchanger conversion step (1) and the anion exchanger conversion step (2) brings the carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water into contact with the mixture that includes the anion exchanger (B) and the cation exchanger, or the mixed bed that includes the anion exchanger (B) and the cation exchanger, until the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion exchanger (A) preferably reaches 50 eq% or more, more preferably 60 eq% or more, still more preferably 70 eq% or more, still more preferably 80 eq% or more, still more preferably 95 eq% or more, still more preferably 99 eq% or more, and still more preferably 100 eq%.

25 [0057]

The ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form included in the anion exchanger (A) that is obtained by the anion exchanger conversion step (1) and the anion exchanger conversion step (2) is preferably 70 eq% or more, more preferably 75 eq% or more, and particularly preferably 80 eq% or more. Since the selectivity coefficient of the bicarbonate form is smaller than that of the carbonate form, the bicarbonate form is effective for improving the treatment performance with respect to an anion having low selectivity, and a low-concentration ion exchange load. The capability to purify a hydrogen peroxide solution and the like increases as the ratio of the bicarbonate form in the anion exchanger increases. Specifically, the capability to purify a hydrogen peroxide solution and the like increases when the ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form included in the anion exchanger (A) is within the above range.

[0058]

In the anion exchanger conversion step (1), the mixture that includes the anion exchanger (B) and the cation exchanger may be put in a container that is provided with a carbon dioxide aqueous solution supply pipe and a carbon dioxide aqueous solution discharge pipe, and the carbon dioxide aqueous solution may be continuously brought into contact with the mixture that includes the anion exchanger (B) and the cation exchanger while supplying the carbon dioxide aqueous solution to the container, and discharging water from the container, for example. In this case, the electrical conductivity of the carbon dioxide aqueous solution is measured before and after the carbon dioxide aqueous solution is brought into contact with the mixture that includes the anion exchanger (B) and the cation exchanger using a conductivity meter that is provided to the carbon dioxide aqueous solution supply pipe and the carbon dioxide aqueous solution discharge pipe, for example, and the carbon dioxide aqueous solution is brought into contact with the mixture that includes the anion exchanger (B) and the

cation exchanger until the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the mixture that includes the anion exchanger (B) and the cation exchanger to the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the mixture that includes the anion exchanger (B) and the cation exchanger ((electrical conductivity after contact / electrical conductivity before contact) $\times$ 100)) reaches 90% or more (preferably 95% or more). It is possible to easily determine the timing of completion of the anion exchanger conversion step (1) by bringing the carbon dioxide aqueous solution into contact with the mixture that includes the anion exchanger (B) and the cation exchanger while calculating a change in the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the mixture that includes the anion exchanger (B) and the cation exchanger to the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the mixture that includes the anion exchanger (B) and the cation exchanger. In the anion exchanger conversion step (1), the majority of carbon dioxide (bicarbonate ions or carbonate ions produced due to the dissolution of carbon dioxide in water) included in the carbon dioxide aqueous solution is consumed due to the ion-exchange reaction of the anion exchanger (B) with the bicarbonate form or the carbonate form for a while after starting to bring the carbon dioxide aqueous solution into contact with the mixture that includes the anion exchanger (B) and the cation exchanger, and the bicarbonate ion concentration or the carbonate ion concentration in the carbon dioxide aqueous solution decreases to a large extent. Therefore, the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the mixture that includes the anion exchanger (B) and the cation exchanger is very low for a while after starting to bring the carbon dioxide aqueous solution into contact with the mixture that includes the anion exchanger (B) and the cation exchanger. The amount of carbon dioxide consumed for the ion-exchange reaction with the bicarbonate form or the

carbonate form gradually decreases as the ion-exchange reaction of the anion exchanger into the bicarbonate form or the carbonate form proceeds, and the amount of anion-exchange groups that have undergone the ion-exchange reaction increases. Therefore, the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the mixture that includes the anion exchanger (B) and the cation exchanger gradually increases since the bicarbonate ion concentration or the carbonate ion concentration in the carbon dioxide aqueous solution gradually increases. It is determined that the majority of the anion-exchange groups included in the anion exchanger (B) have been converted into the bicarbonate form or the carbonate form (i.e., the anion exchanger (A) has been obtained) when the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the mixture that includes the anion exchanger (B) and the cation exchanger to the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the mixture that includes the anion exchanger (B) and the cation exchanger ((electrical conductivity after contact / electrical conductivity before contact) $\times$ 100)) has reached the above range. Note that the electrical conductivity when the carbon dioxide aqueous solution has been brought into contact with the mixture that includes the anion exchanger (B) and the cation exchanger for a certain time, and the electrical conductivity has become almost constant, is taken as the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the mixture that includes the anion exchanger (B) and the cation exchanger in the anion-exchange resin conversion step (anion exchanger conversion step).

[0059]

In the anion exchanger conversion step (2), a conductivity meter may be provided to the inlet and the outlet of the ion exchange column, and the carbon dioxide aqueous solution may be supplied to the ion exchange column until the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange

column to the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column ((electrical conductivity at outlet / electrical conductivity at inlet) $\times$ 100)) reaches 90% or more (preferably 95% or more). It is possible to easily determine the timing of completion of the anion exchanger conversion step (2) by

5 supplying the carbon dioxide aqueous solution to the ion exchange column while calculating a change in the ratio of the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column to the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column. In the anion exchanger conversion step (2), the majority of carbon dioxide (bicarbonate ions or

10 carbonate ions produced due to the dissolution of carbon dioxide in water) included in the carbon dioxide aqueous solution is consumed due to the ion-exchange reaction of the anion exchanger (B) with the bicarbonate form or the carbonate form for a while after starting to bring the carbon dioxide aqueous solution into contact with the mixed bed that includes the anion exchanger (B) and the cation exchanger, and the bicarbonate

15 ion concentration or the carbonate ion concentration in the carbon dioxide aqueous solution decreases to a large extent. Therefore, the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column is very low for a while after starting to bring the carbon dioxide aqueous solution into contact with the mixed bed that includes the anion exchanger (B) and the cation exchanger. The

20 amount of carbon dioxide consumed for the ion-exchange reaction with the bicarbonate form or the carbonate form gradually decreases as the ion-exchange reaction of the anion exchanger into the bicarbonate form or the carbonate form proceeds, and the amount of anion-exchange groups that have undergone the ion-exchange reaction increases. Therefore, the electrical conductivity of the carbon dioxide aqueous

25 solution at the outlet of the ion exchange column gradually increases since the bicarbonate ion concentration or the carbonate ion concentration in the carbon dioxide aqueous solution at the outlet of the ion exchange column gradually increases. It is

determined that the majority of the anion-exchange groups included in the anion exchanger (B) have been converted into the bicarbonate form or the carbonate form (i.e., the anion exchanger (A) has been obtained) when the ratio of the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column to the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column ((electrical conductivity at outlet / electrical conductivity at inlet) × 100)) has reached the above range. Note that the electrical conductivity when the carbon dioxide aqueous solution has been brought into contact with the mixed bed that includes the anion exchanger (B) and the cation exchanger for a certain time, and the electrical conductivity has become almost constant, is taken as the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column in the anion-exchange resin conversion step (anion exchanger conversion step). [0060]

When continuously bringing the carbon dioxide aqueous solution into contact with the mixture that includes the anion exchanger (B) and the cation exchanger, or the mixed bed that includes the anion exchanger (B) and the cation exchanger, to convert the anion exchanger (B) into the anion exchanger (A), the conversion performance increases as the number of anion-exchange groups that are converted into the bicarbonate form or the carbonate form increases based on the total number of anion-exchange groups included in the anion exchanger. Therefore, when converting the anion exchanger (B) into the anion exchanger (A), it is preferable to bring the carbon dioxide aqueous solution into contact with the mixture that includes the anion exchanger (B) and the cation exchanger, or the mixed bed that includes the anion exchanger (B) and the cation exchanger, until the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger reaches 80 eq% or more (particularly preferably 95 eq% or more).

[0061]

The exchange capacity of the anion-exchange groups included in the anion exchanger (before bringing the carbon dioxide aqueous solution into contact with the anion exchanger) that do not have the bicarbonate form or the carbonate form can be calculated by analyzing the anion exchanger before bringing the carbon dioxide aqueous solution into contact with the anion exchanger. If the entirety of the supplied carbon dioxide is used for the ion-exchange reaction, it is possible to obtain an anion exchanger in which the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger is 100 eq% by supplying the carbon dioxide aqueous solution to the anion exchanger until the amount (equivalents/l - anion exchanger) calculated by “carbon dioxide concentration (equivalents/l) in carbon dioxide aqueous solution $\times$ space velocity (SV) (l/l-anion exchanger) $\times$ passing time (h)” (expression (1)) reaches the exchange capacity (equivalents/l-anion exchanger) of the anion-exchange groups included in the anion exchanger that do not have the bicarbonate form or the carbonate form. However, the entirety of the supplied carbon dioxide is not necessarily used for the ion-exchange reaction, and part of the carbon dioxide is necessarily discharged without being used for the ion-exchange reaction since the supplied carbon dioxide is not sufficiently dissolved (i.e., a given concentration is not reached), or leakage of part of the carbon dioxide aqueous solution occurs due to the ion exchange equilibrium, for example. Therefore, it is necessary to set the supply amount of the carbon dioxide aqueous solution to be in excess with respect to the supply amount of the carbon dioxide aqueous solution when the value calculated by the expression (1) reaches the exchange capacity of the anion-exchange groups that do not have the bicarbonate form or the carbonate form so that the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger is 80 eq% or more (preferably

95 eq% or more).

[0062]

However, since it is impossible to remove the anion exchanger and analyze the amount of bicarbonate form and carbonate form during the anion exchanger conversion step (1) or the anion exchanger conversion step (2), it is difficult to determine the amount of the carbon dioxide aqueous solution required to adjust the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger to 80 eq% or more (preferably 95 eq% or more) when the supply amount of the carbon dioxide aqueous solution is merely controlled. Specifically, it is necessary to supply the carbon dioxide aqueous solution in large excess so that the anion-exchange groups are reliably converted, and the carbon dioxide aqueous solution is wasted.

[0063]

It is possible to determine the timing at which the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger reaches 80 eq% or more (preferably 95 eq% or more) by measuring the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger and the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger, calculating the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger to the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger, and supplying the carbon dioxide aqueous solution until the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger to the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger reaches 90% or more (preferably

95% or more). It is also possible to adjust the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger to 80 eq% or more (preferably 95 eq% or more) while supplying a moderate amount of the carbon dioxide aqueous solution (i.e., it is possible to prevent a situation in which the carbon dioxide aqueous solution is wasted).

[0064]

The method for producing an anion exchanger-cation exchanger mixture according to one embodiment of the invention produces a mixture that includes the anion exchanger (A) and the cation exchanger by thus performing the anion exchanger conversion step (1). The method for producing an anion exchanger-cation exchanger mixed bed according to one embodiment of the invention produces a mixed bed that includes the anion exchanger (A) and the cation exchanger by thus performing the anion exchanger conversion step (2). Since the method for producing an anion exchanger-cation exchanger mixture according to one embodiment of the invention and the method for producing an anion exchanger-cation exchanger mixed bed according to one embodiment of the invention utilizes the carbon dioxide aqueous solution to convert the anion-exchange group included in the anion exchanger (B) into the bicarbonate form or the carbonate form without using a carbonate or hydrogen carbonate aqueous solution, it is possible to prevent a situation in which the cation of the cation-exchange group of the cation exchanger used in combination with the anion exchanger is exchanged with the cation of carbonate or hydrogen carbonate.

[0065]

An anion exchanger-cation exchanger mixture according to one embodiment of the invention is a mixture that is obtained by the anion exchanger conversion step (1) and includes the anion exchanger (A) and the cation exchanger. An anion exchanger-cation exchanger mixed bed according to one embodiment of the invention is

a mixed bed that is obtained by the anion exchanger conversion step (2) and includes the anion exchanger (A) and the cation exchanger.

[0066]

A method for purifying a hydrogen peroxide solution according to a first
5 embodiment of the invention includes an anion exchanger conversion step (2) that brings a carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water into contact with a mixed bed that is packed in an ion exchange column and includes an anion exchanger (B) and a cation exchanger to convert the anion exchanger (B) into an anion exchanger (A) that includes the
10 bicarbonate form, or includes the bicarbonate form and the carbonate form, to obtain a mixed bed that includes the anion exchanger (A) and the cation exchanger, and a hydrogen peroxide solution purification step that supplies a crude hydrogen peroxide solution to the ion exchange column so that the crude hydrogen peroxide solution is brought into contact with the mixed bed that includes the anion exchanger (A) and the
15 cation exchanger to obtain a purified hydrogen peroxide solution.

[0067]

Specifically, the method for purifying a hydrogen peroxide solution according to the first embodiment of the invention brings the carbon dioxide aqueous solution into contact with the anion exchanger (B) in the presence of the cation exchanger to convert
20 the anion exchanger (B) into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form (anion exchanger conversion step), and supplies the crude hydrogen peroxide solution to the ion exchange column to purify the crude hydrogen peroxide solution.

[0068]

25 The anion exchanger conversion step (2) included in the method for purifying a hydrogen peroxide solution according to the first embodiment of the invention is the same as the anion exchanger conversion step (2) that is included in the method for

producing an anion exchanger-cation exchanger mixed bed according to one embodiment of the invention. Specifically, the anion exchanger (B), the anion exchanger (A), the cation exchanger, the purified water, the ultrapure water, the carbon dioxide, the dioxide aqueous solution, the mixed bed that includes the anion exchanger (B) and the cation exchanger, and the mixed bed that includes the anion exchanger (A) and the cation exchanger that are used (obtained) in connection with the method for purifying a hydrogen peroxide solution according to the first embodiment of the invention are respectively the same as the anion exchanger (B), the anion exchanger (A), the cation exchanger, the purified water, the ultrapure water, the carbon dioxide, the dioxide aqueous solution, the mixed bed that includes the anion exchanger (B) and the cation exchanger, and the mixed bed that includes the anion exchanger (A) and the cation exchanger that are used (obtained) in connection with the method for producing an anion exchanger-cation exchanger mixed bed according to one embodiment of the invention.

[0069]

When implementing the method for purifying a hydrogen peroxide solution according to the first embodiment of the invention, the anion exchanger conversion step (2) is performed. The anion exchanger conversion step (2) brings the carbon dioxide aqueous solution into contact with the mixed bed that is packed in an ion exchange column and includes the anion exchanger (B) and the cation exchanger to convert the anion exchanger (B) included in the mixed bed packed in the ion exchange column into the anion exchanger (A).

[0070]

When implementing the method for purifying a hydrogen peroxide solution according to the first embodiment of the invention, the hydrogen peroxide solution purification step is performed after the anion exchanger conversion step (2). The hydrogen peroxide solution purification step supplies the crude hydrogen peroxide

solution to the ion exchange column that is packed with the mixed bed that includes the anion exchanger (A) and the cation exchanger so that the crude hydrogen peroxide solution is brought into contact with the mixed bed that includes the anion exchanger (A) and the cation exchanger to obtain a purified hydrogen peroxide solution.

5 [0071]

In the hydrogen peroxide solution purification step, the crude hydrogen peroxide solution is preferably brought into contact with the mixed bed that includes the anion exchanger (A) and the cation exchanger at -10 to 25°C, and particularly preferably -5 to 10°C. In the hydrogen peroxide solution purification step, the crude hydrogen
10 peroxide solution is preferably supplied to the ion exchange column at a space velocity (SV) of 1 to 30 h⁻¹, and particularly preferably 1 to 15 h⁻¹.

[0072]

The method for purifying a hydrogen peroxide solution according to the first embodiment of the invention thus purifies the crude hydrogen peroxide solution.

15 [0073]

When most of the bicarbonate ions (counter anions) included in the anion exchanger (A) have been exchanged with impurity anions included in the crude hydrogen peroxide solution as a result of continuously performing the hydrogen peroxide solution purification step included in the method for purifying a hydrogen
20 peroxide solution according to the first embodiment of the invention, the anion exchanger conversion step (2) may be performed again to convert the anion exchanger (anion exchanger (B)) included in the mixed bed that is packed in the ion exchange column and includes the anion exchanger and the cation exchanger into the anion exchanger (A), and the hydrogen peroxide solution purification step may then be
25 performed. Specifically, when implementing the method for purifying a hydrogen peroxide solution according to the first embodiment of the invention, the anion exchanger conversion step (2) and the hydrogen peroxide solution purification step may

be repeated alternately.

[0074]

The anion exchanger conversion step (2) included in the method for purifying a hydrogen peroxide solution according to the first embodiment of the invention is preferably performed so that the ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form included in the anion exchanger (A) is 70 eq% or more, more preferably 75 eq% or more, and particularly preferably 80 eq% or more. When implementing the anion exchanger conversion step (2) included in the method for purifying a hydrogen peroxide solution according to the first embodiment of the invention, the carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water is preferably brought into contact with the mixed bed that includes the anion exchanger (B) and the cation exchanger until the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion exchanger (A) reaches 50 eq% or more, preferably 60 eq% or more, more preferably 70 eq% or more, still more preferably 80 eq% or more, still more preferably 95 eq% or more, still more preferably 99 eq% or more, and still more preferably 100 eq%.

[0075]

When implementing the anion exchanger conversion step (2) included in the method for purifying a hydrogen peroxide solution according to the first embodiment of the invention, a conductivity meter may be provided to the inlet and the outlet of the ion exchange column, and the carbon dioxide aqueous solution may be supplied to the ion exchange column until the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column to the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column ((electrical conductivity at outlet / electrical conductivity at inlet) $\times$ 100)) reaches 90% or more (preferably 95% or more).

[0076]

It is possible to determine the timing at which the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger reaches 80 eq% or more (preferably 95 eq% or more) by measuring the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger and the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger, calculating the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger to the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger, and supplying the carbon dioxide aqueous solution until the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger to the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger reaches 90% or more (preferably 95% or more). It is also possible to adjust the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger to 80 eq% or more (preferably 95 eq% or more) while supplying a moderate amount of the carbon dioxide aqueous solution (i.e., it is possible to prevent a situation in which the carbon dioxide aqueous solution is wasted).

[0077]

An anion exchanger according to one embodiment of the invention is an anion exchanger that includes a bicarbonate form (-HCO_3), or an anion exchanger that includes a bicarbonate form (-HCO_3) and a carbonate form (-CO_3). Specifically, the anion exchanger according to one embodiment of the invention is the same as the anion exchanger (A) that is used in connection with the anion exchanger-cation exchanger

mixture according to one embodiment of the invention and the anion exchanger-cation exchanger mixed bed according to one embodiment of the invention. Therefore, the anion exchanger according to one embodiment of the invention may be hereinafter referred to as “anion exchanger (A)”.

5 [0078]

The anion exchanger according to one embodiment of the invention (anion exchanger (A)) is an anion exchanger that includes a bicarbonate form (-HCO_3), or an anion exchanger that includes a bicarbonate form (-HCO_3) and a carbonate form (-CO_3) (i.e., an anion exchanger that includes an anion-exchange group of which the counter

10 anion is a bicarbonate ion (-HCO_3 ion), or an anion exchanger that includes an anion-exchange group of which the counter anion is a bicarbonate ion (-HCO_3 ion), and an anion-exchange group of which the counter anion is a carbonate ion (-CO_3 ion)).

The anion exchanger (A) is an anion exchanger that includes a resin as a base, and includes an anion-exchange group that is introduced into the resin. The anion

15 exchanger (A) is a styrene-based gel-type or MR-type anion-exchange resin or organic porous anion exchanger. With regard to the expressions “bicarbonate form (R-HCO_3)” and “carbonate form (R-CO_3)” used herein, the carbonate form is present in the form of R-HCO_3^- , and the bicarbonate form is present in the form of R-CO_3^{2-} under actual usage conditions.

20 [0079]

The ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form included in the anion exchanger according to one embodiment of the invention (anion exchanger (A)) is preferably 70 eq% or more, more preferably 75 eq% or more, and particularly

25 preferably 80 eq% or more. When the ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form is within the above range, it is possible to obtain a high capability to

purify a hydrogen peroxide solution, water, an aqueous solution, or an organic solvent that is purified using an anion exchanger.

[0080]

The anion exchanger according to one embodiment of the invention (anion exchanger (A)) may further have an ionic form other than the bicarbonate form and the carbonate form as long as purification is not adversely affected. It is preferable that the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion exchanger be 50 eq% or more, more preferably 60 eq% or more, still more preferably 70 eq% or more, still more preferably 80 eq% or more, still more preferably 95 eq% or more, still more preferably 99 eq% or more, and still more preferably 100 eq%. When the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion exchanger is within the above range, it is possible to obtain a high capability to purify a hydrogen peroxide solution, water, an aqueous solution, or an organic solvent that is purified using an anion exchanger.

[0081]

When the anion exchanger according to one embodiment of the invention (anion exchanger (A)) further has an ionic form other than the bicarbonate form and the carbonate form, the ionic form other than the bicarbonate form and the carbonate form may be a Cl form, an OH form, or the like. Note that the decomposition reaction of hydrogen peroxide may easily proceed when purifying a hydrogen peroxide solution if the content of OH form in the anion exchanger (A) is too high. Therefore, when the anion exchanger (A) is used to purify hydrogen peroxide, the ratio of the exchange capacity of the OH form to the total exchange capacity of the anion exchanger (A) is preferably 1 eq% or less, more preferably 0.1 eq% or less, and particularly preferably 0 eq%.

[0082]

A styrene-divinylbenzene copolymer is preferable as the resin (into which the anion-exchange group is introduced) included in the anion exchanger according to one embodiment of the invention (anion exchanger (A)).

[0083]

5 Examples of the anion exchanger according to one embodiment of the invention (anion exchanger (A)) include a strongly basic type I anion exchanger that includes a quaternary ammonium group as a functional group, wherein only an alkyl group is bonded to the nitrogen atom of the ammonium group; a strongly basic type II anion exchanger that includes a quaternary ammonium group as a functional group, wherein
10 an alkyl group and an alkanol group are bonded to the nitrogen atom of the ammonium group; and a weakly basic anion exchanger that includes a primary to tertiary amino group as a functional group. Among these, the strongly basic type I anion exchanger is preferable.

[0084]

15 When the anion exchanger according to one embodiment of the invention (anion exchanger (A)) is a particulate anion-exchange resin, the average particle size of the anion-exchange resin is preferably 0.2 to 1.0 mm, and particularly preferably 0.4 to 0.8 mm. When the anion exchanger according to one embodiment of the invention (anion exchanger (A)) is an organic porous anion exchanger, the organic porous anion
20 exchanger has a structure in which a number of cell-like macropores overlap each other, and communicating holes formed by the macropores that overlap each other are formed in the skeleton formed of a resin (i.e., continuous macropore structure).

[0085]

 A method for producing an anion exchanger according to one embodiment of the
25 invention includes an anion exchanger conversion step (3) that brings a carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water into contact with an anion exchanger (B) to convert the anion exchanger (B) into

an anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form.

[0086]

The anion exchanger conversion step (3) included in the method for producing an anion exchanger according to one embodiment of the invention brings the carbon dioxide aqueous solution into contact with the anion exchanger (B) to convert the anion exchanger (B) into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form.

[0087]

The anion exchanger (B) used in connection with the anion exchanger conversion step (3) is an anion exchanger that is converted into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form. When a crude hydrogen peroxide solution is purified using an OH-form anion exchanger (i.e., an anion exchanger in which the counter anion of the anion-exchange group is an OH ion) (i.e., strongly basic anion exchanger), hydrogen peroxide is decomposed when hydrogen peroxide is brought into contact with the OH-form anion exchanger. When a crude hydrogen peroxide solution is purified using a Cl-form anion exchanger (i.e., an anion exchanger in which the counter anion of the anion-exchange group is a Cl ion), the Cl ions flow out into the treatment solution due to an ion-exchange reaction with the target ions (i.e., it is impossible to effect purification). Therefore, the method for producing an anion exchanger according to one embodiment of the invention converts the anion exchanger into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form.

[0088]

The anion exchanger conversion step (3) brings the carbon dioxide aqueous solution into contact with an OH-form anion exchanger, a Cl-form anion exchanger, or

the like (preferably an OH-form anion exchanger) (i.e., an anion exchanger (anion exchanger (B)) that is converted into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form) to convert the anion exchanger (B) into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form. When the treatment target water (i.e., a hydrogen peroxide solution, water, or an aqueous solution that is purified using a mixed bed that includes an anion exchanger and a cation exchanger) is continuously purified using the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form, the bicarbonate ions included in the anion exchanger (A) are exchanged with impurity anions included in the treatment target water. Therefore, when the treatment target water has been continuously purified for a certain time, it is necessary to regenerate the anion exchanger that has been subjected to the ion-exchange reaction with impurity anions into the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form. The anion exchanger (B) (that is converted into the anion exchanger (A) that includes a bicarbonate form, or includes a bicarbonate form and a carbonate form) that is subjected to the anion exchanger conversion step (3) that is performed to obtain the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form, includes the anion exchanger that is converted into the anion exchanger (A), and the anion exchanger that has been subjected to the ion-exchange reaction with impurity anions included in the treatment target water during the purification of the treatment target water (e.g., hydrogen peroxide solution), and is subjected again to the anion exchanger conversion step (3). [0089]

25 The anion exchanger (A) obtained by the anion exchanger conversion step (3) is an anion exchanger that includes a bicarbonate form (-HCO_3), or an anion exchanger that includes a bicarbonate form (-HCO_3) and a carbonate form (-CO_3). The ratio of

the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion exchanger (A) is not particularly limited, but is preferably 50 eq% or more, more preferably 60 eq% or more, still more preferably 70 eq% or more, still more preferably 80 eq% or more, still more preferably 95 eq% or more, still more preferably 99 eq% or more, and still more preferably 100 eq%. The ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form is preferably 70 eq% or more, more preferably 75 eq% or more, and particularly preferably 80 eq% or more.

[0090]

10 The anion exchanger (B) that is subjected to the anion exchanger conversion step (3) is an anion exchanger that includes a resin as a base, and includes an anion-exchange group that is introduced into the resin. The anion exchanger (B) is a styrene-based gel-type or MR-type anion-exchange resin or organic porous anion exchanger. A styrene-divinylbenzene copolymer is preferable as the resin (into which
15 the anion-exchange group is introduced) included in the anion exchanger (B).

[0091]

Examples of the anion exchanger (B) that is subjected to the anion exchanger conversion step (3) include a strongly basic type I anion exchanger that includes a quaternary ammonium group as a functional group, wherein only an alkyl group is
20 bonded to the nitrogen atom of the ammonium group; a strongly basic type II anion exchanger that includes a quaternary ammonium group as a functional group, wherein an alkyl group and an alkanol group are bonded to the nitrogen atom of the ammonium group; and a weakly basic anion exchanger that includes a primary to tertiary amino group as a functional group. Among these, the strongly basic type I anion exchanger is
25 preferable. An OH-form anion exchanger is preferable as the anion exchanger (B) that is subjected to the anion exchanger conversion step (3).

[0092]

When the anion exchanger (B) that is subjected to the anion exchanger conversion step (3) is a particulate anion-exchange resin, the average particle size of the anion-exchange resin is preferably 0.2 to 1.0 mm, and particularly preferably 0.4 to 0.8 mm. When the anion-exchange resin (anion exchanger) (B) that is subjected to the anion exchanger conversion step (3) is an organic porous anion exchanger, the organic porous anion exchanger has a structure in which a number of cell-like macropores overlap each other, and communicating holes formed by the macropores that overlap each other are formed in the skeleton formed of a resin (i.e., continuous macropore structure).

10 [0093]

The carbon dioxide aqueous solution that is used in connection with the anion exchanger conversion step (3) is obtained by dissolving carbon dioxide in purified water or ultrapure water. The purified water or the ultrapure water is obtained by treating raw water using a water purifier or an ultrapure water system that removes ions and a non-ionic substance from raw water. It is preferable to use purified water having a resistivity of 1.0 MΩ·cm or more, more preferably ultrapure water having a resistivity of 10 MΩ·cm or more, and particularly preferably ultrapure water having a resistivity of 18 MΩ·cm or more.

[0094]

20 The carbon dioxide concentration in the carbon dioxide aqueous solution that is used in connection with the anion exchanger conversion step (3) is not particularly limited (as long as carbon dioxide is dissolved in purified water or ultrapure water), but is preferably 1 to 2,000 mg/L, and particularly preferably 20 to 2,000 mg/L. It is possible to reduce the treatment time and the amount of water used by increasing the carbon dioxide concentration in the carbon dioxide aqueous solution.

25 [0095]

The carbon dioxide aqueous solution may be prepared (i.e., carbon dioxide may

be dissolved in purified water or ultrapure water) using an arbitrary method. For example, the carbon dioxide aqueous solution may be prepared using a method for producing functional water that is used for washing electronic parts. For example, the carbon dioxide aqueous solution may be prepared using a method that dissolves carbon dioxide using a hollow fiber membrane, a method that bubbles carbon dioxide directly into a pipe, a method that injects carbon dioxide, and dissolves the carbon dioxide using a dispersion means such as a static mixer, a method that supplies carbon dioxide to a gas dissolution tank on the upstream side of a pump that supplies ultrapure water, and dissolves the carbon dioxide by stirring inside the pump, or the like. It is preferable to dissolve carbon dioxide using a hollow fiber membrane in order to efficiently dissolve carbon dioxide up to the saturation concentration. When using a gas cylinder in order to supply carbon dioxide, it is preferable to provide a particulate removal filter that removes microparticles having a particle size of 0.5 μm or less in a gas supply pipe. It is particularly preferable to provide a particulate removal filter that removes microparticles having a particle size of 0.2 μm or less.

[0096]

When preparing the carbon dioxide aqueous solution, the supply amount of carbon dioxide that is dissolved in purified water or ultrapure water is controlled using a gas mass flow controller. The carbon dioxide concentration is continuously monitored using a conductivity meter.

[0097]

In the anion exchanger conversion step (3), the carbon dioxide aqueous solution may be brought into contact with the anion exchanger (B) using an arbitrary method. For example, the carbon dioxide aqueous solution may be brought into contact with the anion exchanger (B) using a method that adds the anion exchanger (B) to the carbon dioxide aqueous solution, and stirs the mixture, a method that puts the anion exchanger (B) in a contact container provided with a carbon dioxide aqueous solution supply pipe

and a carbon dioxide aqueous solution discharge pipe, and discharges water from the container while supplying the carbon dioxide aqueous solution to the container, a method that packs an ion exchange column with the anion exchanger (B), and supplies the carbon dioxide aqueous solution to the ion exchange column. The temperature at which the carbon dioxide aqueous solution is brought into contact with the anion exchanger (B) in the anion exchanger conversion step (3) is preferably set to be as low as possible in order to increase the solubility of carbon dioxide, but is preferably 5 to 40°C, and particular preferably 10 to 30°C, from the viewpoint of energy consumption. When the carbon dioxide aqueous solution is passed through an ion exchange column that is packed with the anion exchanger (B) in the anion exchanger conversion step (3), the carbon dioxide aqueous solution may be supplied to the ion exchange column by a single-pass operation. Note that a recycle tank and a recycle pump may be provided in the subsequent stage of the ion exchange column, and the used water may be recycled as raw water for preparing the carbon dioxide aqueous solution in order to reduce the amount of purified water or ultrapure water to be used. When recycling water, the amount of carbon dioxide to be supplied can be reduced by feeding back the value measured by a conductivity meter, and controlling the amount of carbon dioxide to be supplied.

[0098]

In the anion exchanger conversion step (3), some or all of the counter anions included in the anion exchanger (B) are converted into a bicarbonate ion (-HCO_3) or a carbonate ion (-CO_3) to obtain the anion exchanger (A) that includes the bicarbonate form, or includes the bicarbonate form and the carbonate form.

[0099]

The anion exchanger (A) that is obtained by the anion exchanger conversion step (3) is an anion exchanger that includes a bicarbonate form (-HCO_3), or an anion exchanger that includes a bicarbonate form (-HCO_3) and a carbonate form (-CO_3) (i.e.,

an anion exchanger that includes an anion-exchange group of which the counter anion is a bicarbonate ion (-HCO_3 ion), or an anion exchanger that includes an anion-exchange group of which the counter anion is a bicarbonate ion (-HCO_3 ion), and an anion-exchange group of which the counter anion is a carbonate ion (-CO_3 ion)). With regard to the expressions “bicarbonate form (R-HCO_3)” and “carbonate form (R-CO_3)” used herein, the carbonate form is present in the form of R-HCO_3^- , and the bicarbonate form is present in the form of R-CO_3^{2-} under actual usage conditions.

[0100]

The ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger (A) (that is obtained by the anion exchanger conversion step (3)) is not particularly limited, but is preferably 50 eq% or more, more preferably 60 eq% or more, still more preferably 70 eq% or more, still more preferably 80 eq% or more, still more preferably 95 eq% or more, still more preferably 99 eq% or more, and still more preferably 100 eq%. Specifically, when implementing the anion exchanger conversion step (3), the carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water is preferably brought into contact with the anion exchanger (B) until the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger (A) reaches 50 eq% or more, preferably 60 eq% or more, more preferably 70 eq% or more, still more preferably 80 eq% or more, still more preferably 95 eq% or more, still more preferably 99 eq% or more, and still more preferably 100 eq%.

[0101]

The ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form included in the anion exchanger (A) that is obtained by the anion exchanger conversion step (3) is preferably

70 eq% or more, more preferably 75 eq% or more, and particularly preferably 80 eq% or more. Since the selectivity coefficient of the bicarbonate form is smaller than that of the carbonate form, the bicarbonate form is effective for improving the treatment performance with respect to an anion having low selectivity, and a low-concentration ion exchange load. The capability to purify a hydrogen peroxide solution and the like increases as the ratio of the bicarbonate form in the anion exchanger increases. Specifically, the capability to purify a hydrogen peroxide solution and the like increases when the ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form included in the anion exchanger (A) is within the above range.

[0102]

In the anion exchanger conversion step (3), the anion exchanger (B) may be put in a container that is provided with a carbon dioxide aqueous solution supply pipe and a carbon dioxide aqueous solution discharge pipe, and the carbon dioxide aqueous solution may be continuously brought into contact with the anion exchanger (B) while supplying the carbon dioxide aqueous solution to the container, and discharging water from the container, or packing an ion exchange column with the anion exchanger (B), and discharging water from the ion exchange column while supplying the carbon dioxide aqueous solution to the ion exchange column, for example. In this case, the electrical conductivity of the carbon dioxide aqueous solution is measured before and after the carbon dioxide aqueous solution is brought into contact with the anion exchanger (B), and the carbon dioxide aqueous solution is brought into contact with the anion exchanger (B) until the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger (B) to the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger (B) ((electrical conductivity after contact / electrical conductivity before contact) $\times$ 100)) reaches 90% or more (preferably 95% or more).

It is possible to easily determine the timing of completion of the anion exchanger conversion step (3) by bringing the carbon dioxide aqueous solution into contact with the anion exchanger (B) while calculating a change in the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger (B) to the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger (B). In the anion exchanger conversion step (3), the majority of carbon dioxide (bicarbonate ions or carbonate ions produced due to the dissolution of carbon dioxide in water) included in the carbon dioxide aqueous solution is consumed due to the ion-exchange reaction of the anion-exchange resin (anion exchanger) (B) with the bicarbonate form or the carbonate form for a while after starting to bring the carbon dioxide aqueous solution into contact with the anion exchanger (B), and the bicarbonate ion concentration or the carbonate ion concentration in the carbon dioxide aqueous solution decreases to a large extent. Therefore, the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger (B) is very low for a while after starting to bring the carbon dioxide aqueous solution into contact with the anion exchanger (B). The amount of carbon dioxide consumed for the ion-exchange reaction with the bicarbonate form or the carbonate form gradually decreases as the ion-exchange reaction of the anion-exchange resin (anion exchanger) into the bicarbonate form or the carbonate form proceeds, and the amount of anion-exchange groups that have undergone the ion-exchange reaction increases. Therefore, the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger (B) gradually increases since the bicarbonate ion concentration or the carbonate ion concentration in the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger (B) gradually increases. It is determined that the majority of the anion-exchange groups included in the anion exchanger (B) have been converted into the bicarbonate form or

the carbonate form (i.e., the anion exchanger (A) has been obtained) when the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger (B) to the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger (B) ((electrical conductivity after contact / electrical conductivity before contact) × 100)) has reached the above range. Note that the electrical conductivity when the carbon dioxide aqueous solution has been brought into contact with the anion exchanger (B) for a certain time, and the electrical conductivity has become almost constant, is taken as the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger (B) in the anion-exchange resin conversion step (anion exchanger conversion step) (3).

[0103]

When continuously bringing the carbon dioxide aqueous solution into contact with the anion exchanger (B) to convert the anion exchanger (B) into the anion exchanger (A), the conversion performance increases as the number of anion-exchange groups that are converted into the bicarbonate form or the carbonate form increases based on the total number of anion-exchange groups included in the anion exchanger in the same manner as in the anion exchanger conversion step (1) and the anion exchanger conversion step (2). Therefore, when converting the anion exchanger (B) into the anion exchanger (A), it is preferable to bring the carbon dioxide aqueous solution into contact with the anion exchanger (B) until the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger reaches 80 eq% or more (particularly preferably 95 eq% or more).

[0104]

The exchange capacity of the anion-exchange groups included in the anion exchanger (before bringing the carbon dioxide aqueous solution into contact with the

anion exchanger) that do not have the bicarbonate form or the carbonate form can be calculated by analyzing the anion exchanger before bringing the carbon dioxide aqueous solution into contact with the anion exchanger. If the entirety of the supplied carbon dioxide is used for the ion-exchange reaction, it is possible to obtain an anion exchanger in which the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger is 100 eq% by supplying the carbon dioxide aqueous solution to the anion exchanger until the amount (equivalents/l - anion exchanger) calculated by “carbon dioxide concentration (equivalents/l) in carbon dioxide aqueous solution × space velocity (SV) (l/l-anion exchanger) × passing time (h)” (expression (1)) reaches the exchange capacity (equivalents/l-anion exchanger) of the anion-exchange groups included in the anion exchanger that do not have the bicarbonate form or the carbonate form. However, the entirety of the supplied carbon dioxide is not necessarily used for the ion-exchange reaction, and part of the carbon dioxide is necessarily discharged without being used for the ion-exchange reaction since the supplied carbon dioxide is not sufficiently dissolved (i.e., a given concentration is not reached), or leakage of part of the carbon dioxide aqueous solution occurs due to the ion exchange equilibrium, for example. Therefore, it is necessary to set the supply amount of the carbon dioxide aqueous solution to be in excess with respect to the supply amount of the carbon dioxide aqueous solution when the value calculated by the expression (1) reaches the exchange capacity of the anion-exchange groups that do not have the bicarbonate form or the carbonate form so that the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger is 80 eq% or more (preferably 95 eq% or more).

[0105]

However, since it is impossible to remove the anion exchanger and analyze the amount of bicarbonate form and carbonate form during the anion exchanger conversion

step (3), it is difficult to determine the amount of the carbon dioxide aqueous solution required to adjust the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger to 80 eq% or more (preferably 95 eq% or more) when the supply amount of the carbon dioxide aqueous solution is merely controlled.

Specifically, it is necessary to supply the carbon dioxide aqueous solution in large excess so that the anion-exchange groups are reliably converted, and the carbon dioxide aqueous solution is wasted.

[0106]

It is possible to determine the timing at which the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger reaches 80 eq% or more (preferably 95 eq% or more) by measuring the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger and the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger, calculating the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger to the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger, and supplying the carbon dioxide aqueous solution until the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger to the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger reaches 90% or more (preferably 95% or more). It is also possible to adjust the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger to 80 eq% or more (preferably 95 eq% or more) while supplying a moderate amount of the carbon dioxide aqueous

solution (i.e., it is possible to prevent a situation in which the carbon dioxide aqueous solution is wasted).

[0107]

A method for purifying a hydrogen peroxide solution according to a second
5 embodiment of the invention includes an anion exchanger conversion step (4) that
brings a carbon dioxide aqueous solution obtained by dissolving carbon dioxide in
purified water or ultrapure water into contact with an anion exchanger (B) that is packed
in an ion exchange column to convert the anion exchanger (B) into an anion exchanger
(A) that includes the bicarbonate form, or includes the bicarbonate form and the
10 carbonate form, and a hydrogen peroxide solution purification step that supplies a crude
hydrogen peroxide solution to the ion exchange column so that the crude hydrogen
peroxide solution is brought into contact with the anion exchanger (A) to obtain a
purified hydrogen peroxide solution.

[0108]

15 The anion exchanger (B), the anion exchanger (A), the purified water, the
ultrapure water, the carbon dioxide, and the dioxide aqueous solution that are used
(obtained) in connection with the anion exchanger conversion step (4) included in the
method for purifying a hydrogen peroxide solution according to the second embodiment
of the invention are respectively the same as the anion exchanger (B), the anion
20 exchanger (A), the purified water, the ultrapure water, the carbon dioxide, and the
dioxide aqueous solution that are used (obtained) in connection with the anion
exchanger conversion step (3) included in the method for producing an anion exchanger
according to one embodiment of the invention.

[0109]

25 When implementing the method for purifying a hydrogen peroxide solution
according to the second embodiment of the invention, the anion exchanger conversion
step (4) is performed. The anion exchanger conversion step (4) brings the carbon

dioxide aqueous solution into contact with the anion exchanger (B) that is packed in an ion exchange column to convert the anion exchanger (B) packed in the ion exchange column into the anion exchanger (A). In the anion exchanger conversion step (4), the anion exchanger (B) is packed in the ion exchange column, and the carbon dioxide aqueous solution is supplied to the ion exchange column packed with the anion exchanger (B) to bring the carbon dioxide aqueous solution into contact with the anion exchanger (B).

[0110]

When implementing the method for purifying a hydrogen peroxide solution according to the second embodiment of the invention, the hydrogen peroxide solution purification step is performed after the anion exchanger conversion step (4). The hydrogen peroxide solution purification step supplies the crude hydrogen peroxide solution to the ion exchange column that is packed with the anion exchanger (A) so that the crude hydrogen peroxide solution is brought into contact with the anion exchanger (A) to obtain a purified hydrogen peroxide solution.

[0111]

In the hydrogen peroxide solution purification step, the crude hydrogen peroxide solution is preferably brought into contact with the anion exchanger (A) at -10 to 25°C, and particularly preferably -5 to 10°C. In the hydrogen peroxide solution purification step, the crude hydrogen peroxide solution is preferably supplied to the ion exchange column at a space velocity (SV) of 1 to 30 h⁻¹, and particularly preferably 1 to 15 h⁻¹.

[0112]

The method for purifying a hydrogen peroxide solution according to the second embodiment of the invention thus purifies the crude hydrogen peroxide solution.

[0113]

When most of the bicarbonate ions (counter anions) included in the anion exchanger (A) have been exchanged with impurity anions included in the crude

hydrogen peroxide solution as a result of continuously performing the hydrogen peroxide solution purification step included in the method for purifying a hydrogen peroxide solution according to the second embodiment of the invention, the anion exchanger conversion step (4) may be performed again to convert the anion exchanger (anion exchanger (B)) that is packed in the ion exchange column into the anion exchanger (A), and the hydrogen peroxide solution purification step may then be performed. Specifically, when implementing the method for purifying a hydrogen peroxide solution according to the second embodiment of the invention, the anion exchanger conversion step (4) and the hydrogen peroxide solution purification step may be repeated alternately.

[0114]

The anion exchanger conversion step (4) included in the method for purifying a hydrogen peroxide solution according to the second embodiment of the invention is preferably performed so that the ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form included in the anion exchanger (A) is 70 eq% or more, more preferably 75 eq% or more, and particularly preferably 80 eq% or more. When implementing the anion exchanger conversion step (4) included in the method for purifying a hydrogen peroxide solution according to the second embodiment of the invention, the carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water is preferably brought into contact with the anion exchanger (B) until the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion exchanger (A) reaches 50 eq% or more, preferably 60 eq% or more, more preferably 70 eq% or more, still more preferably 80 eq% or more, still more preferably 95 eq% or more, still more preferably 99 eq% or more, and still more preferably 100 eq%.

[0115]

When implementing the anion exchanger conversion step (4) included in the method for purifying a hydrogen peroxide solution according to the second embodiment of the invention, an electrical conductivity meter may be provided to the inlet and the outlet of the ion exchange column, and the carbon dioxide aqueous solution may be supplied to the ion exchange column until the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column to the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column ((electrical conductivity at outlet / electrical conductivity at inlet) $\times$ 100)) reaches 90% or more (preferably 95% or more).

[0116]

It is possible to determine the timing at which the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger reaches 80 eq% or more (preferably 95 eq% or more) by measuring the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger and the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger, calculating the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger to the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger, and supplying the carbon dioxide aqueous solution until the ratio of the electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the anion exchanger to the electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the anion exchanger reaches 90% or more (preferably 95% or more). It is also possible to adjust the ratio of the total exchange capacity of the bicarbonate form and the carbonate form to the total exchange capacity of the anion-exchange groups included in the anion exchanger to 80 eq% or more (preferably

95 eq% or more) while supplying a moderate amount of the carbon dioxide aqueous solution (i.e., it is possible to prevent a situation in which the carbon dioxide aqueous solution is wasted).

[0117]

5 In the anion exchanger conversion step, the carbon dioxide aqueous solution in which carbon dioxide is dissolved is used to exchange the counter anion of the anion exchanger (B) with the bicarbonate ion. Since the carbon dioxide aqueous solution is weakly acidic, the carbon dioxide aqueous solution includes monovalent bicarbonate ions in a high ratio. Therefore, an anion exchanger in which the ratio of the
10 bicarbonate form is high (i.e., an anion exchanger in which the ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form included in the anion exchanger (A) is 70 eq% or more, preferably 75 eq% or more, and particularly preferably 80 eq% or more) can be obtained by the anion exchanger conversion step.

15 [0118]

 According to a known method, a hydrogen carbonate aqueous solution is used to exchange the counter anion of the anion exchanger. However, since the hydrogen carbonate aqueous solution is weakly alkaline, the hydrogen carbonate aqueous solution includes divalent carbonate ions in a high ratio. Therefore, the ratio of the bicarbonate
20 form is low when using a known method.

[0119]

 Since the ion-exchange capability of the bicarbonate form is higher than that of the carbonate form, an anion exchanger that includes the bicarbonate form in a high ratio exhibits an excellent capability to purify a hydrogen peroxide solution and the like
25 as compared with an anion exchanger that includes the bicarbonate form in a low ratio, and is considered to exhibit improved treatment performance with respect to an anion with low selectivity and low-concentration ion exchange load. According to the

embodiments of the invention, since the anion exchanger conversion step ensures that the ratio of the exchange capacity of the bicarbonate form to the total exchange capacity of the bicarbonate form and the carbonate form reaches 70 eq% or more, preferably 75 eq% or more, and particularly preferably 80 eq% or more, it is possible to obtain an anion exchanger that exhibits an excellent capability to purify the treatment target water (i.e., a hydrogen peroxide solution, water, an aqueous solution, or an organic solvent that is purified using an anion exchanger, or a mixture or a mixed bed that includes an anion exchanger and a cation exchanger), and exhibits improved treatment performance with respect to an anion with low selectivity and low-concentration ion exchange load.

10 [0120]

Therefore, it is possible to increase the amount of treatment target water that can be treated until the next anion exchanger conversion step is performed. Specifically, when the anion exchanger conversion step and the hydrogen peroxide solution purification step are repeated when implementing the method for purifying a hydrogen peroxide solution according to the embodiments of the invention, the frequency of the anion exchanger conversion step can be reduced, and it is possible to efficiently purify a hydrogen peroxide solution.

[0121]

According to the method for purifying a hydrogen peroxide solution according to the embodiments of the invention, the anion exchanger (A) that is used to purify a crude hydrogen peroxide solution is prepared using the carbon dioxide aqueous solution. Since a salt such as ammonium bicarbonate is not dissolved in the carbon dioxide aqueous solution, it is unnecessary to remove ammonium ions after converting the anion exchanger into the bicarbonate form (differing from a known method that uses an ammonium bicarbonate aqueous solution). Specifically, the method for purifying a hydrogen peroxide solution according to the embodiments of the invention can implement the hydrogen peroxide solution purification step immediately after the anion

exchanger conversion step without washing the anion exchanger (A). Therefore, the method for purifying a hydrogen peroxide solution according to the embodiments of the invention can efficiently purify a hydrogen peroxide solution.

5 EXAMPLES

[0122]

The invention is further described below by way of examples. Note that the invention is not limited to the following examples.

[0123]

10 Example 1

An ion exchange column made of PFA (copolymer of tetrafluoroethylene and perfluoroalkyl vinyl ether) (inner diameter: 16 mm, height: 30 cm) (see FIG. 1) was provided with a PFA mesh (at the bottom), and packed with 50 mL of a mixed bed including a strongly basic anion exchanger (OH form) and a strongly acidic cation
15 exchanger (H form) (“ESP-1” manufactured by Organo Corporation, mixed bed ratio: 1:1). Ultrapure water and carbon dioxide (controlled using a gas mass flow controller) were supplied to a gas dissolution hollow fiber membrane, and the carbon dioxide was dissolved in the ultrapure water to obtain a carbon dioxide aqueous solution. The carbon dioxide aqueous solution was supplied to the ion exchange column, and passed
20 through the ESP-1 packed bed. The flow rate inside the ion exchange column was set to 1.5 L/h, and the amount of carbon dioxide supplied to the hollow fiber membrane was adjusted so that the electrical conductivity at the inlet of the ion exchange column was 38 $\mu\text{S}/\text{cm}$. The carbon dioxide aqueous solution was continuously passed through the packed bed until the electrical conductivity at the outlet of the ion exchange column
25 became equal to the electrical conductivity (38 $\mu\text{S}/\text{cm}$) at the inlet of the ion exchange column (about 90 minutes) to obtain a mixed bed A including the anion exchanger and the cation exchanger. FIG. 2 illustrates a change in the electrical conductivity of the

carbon dioxide aqueous solution at the inlet of the ion exchange column and the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column. As illustrated in FIG. 2, the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column changed to some extent for a while after starting to supply the carbon dioxide aqueous solution to the ion exchange column, but became constant ($38 \mu\text{S}/\text{cm}$) when about 45 minutes had elapsed after starting to supply the carbon dioxide aqueous solution.

[0124]

Ultrapure water was supplied to the ion exchange column for 10 minutes, and the water discharged from the ion exchange column was sampled. The ammonium ion concentration in the discharged water was measured, and found to be less than $0.1 \text{ mg}/\text{L}$ (less than the lower detection limit).

[0125]

In order to calculate the ion conversion rate (%) (i.e., the rate of conversion into the carbonate form or the bicarbonate form) of the anion exchanger included in the mixed bed A including the anion exchanger and the cation exchanger, a sodium nitrate aqueous solution was passed through a packed bed, and neutralization titration of the obtained solution was performed using sodium hydroxide (indicator: phenolphthalein-methyl red mixture). The results are shown in Table 1.

[0126]

The relationship between the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column, the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column (see FIG. 2), and the conversion rate (i.e., the rate of conversion into the bicarbonate form, or the bicarbonate form and the carbonate form) of the anion-exchange resin was determined. When the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column had reached $34 \mu\text{S}/\text{cm}$, the electrical conductivity of the

carbon dioxide aqueous solution at the inlet of the ion exchange column was 38 $\mu\text{S}/\text{cm}$, the ratio of the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column to the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column was 90%, and the conversion rate (i.e., the rate of conversion into the bicarbonate form, or the bicarbonate form and the carbonate form) of the anion-exchange resin was 99.3%. When the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column had reached 36 $\mu\text{S}/\text{cm}$, the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column was 38 $\mu\text{S}/\text{cm}$, the ratio of the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column to the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column was 95%, and the conversion rate (i.e., the rate of conversion into the bicarbonate form, or the bicarbonate form and the carbonate form) of the anion-exchange resin was 99.9%. Note that the conversion rate (i.e., the rate of conversion into the bicarbonate form, or the bicarbonate form and the carbonate form) of the anion-exchange resin was calculated as described below. The carbon dioxide load per unit time with respect to the anion-exchange resin was calculated from the difference between the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column and the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column, and integrated corresponding to the passing time to calculate the carbon dioxide load. The total carbon dioxide load when the electrical conductivity of the carbon dioxide aqueous solution at the inlet of the ion exchange column and the electrical conductivity of the carbon dioxide aqueous solution at the outlet of the ion exchange column became identical to each other was calculated, and the conversion rate was calculated by “(carbon dioxide load / total carbon dioxide load) $\times$ 100 (%)”.

[0127]

Comparative Example 1

An ion exchange column made of PFA (inner diameter: 16 mm, height: 30 cm) was provided with a PFA mesh (at the bottom), and packed with 50 mL of a strongly basic type I anion exchanger (“ESG4002” manufactured by Organo Corporation, OH form). Ammonium bicarbonate was dissolved in ultrapure water to obtain a 5% ammonium bicarbonate aqueous solution. The ammonium bicarbonate aqueous solution was supplied to the ion exchange column at a flow rate of 0.25 L/h, and passed through the ESG4002 layer for 3 hours to obtain an anion exchanger a.

[0128]

The ion conversion rate (%) (i.e., the rate of conversion into the carbonate form or the bicarbonate form) of the anion exchanger a was calculated in the same manner as in Example 1. The results are shown in Table 1.

[0129]

Comparative Example 2

An anion exchanger b was obtained in the same manner as in Comparative Example 1, except that the concentration of the ammonium bicarbonate aqueous solution was changed to 0.8%, and the ammonium bicarbonate aqueous solution was passed through the ESG4002 layer for 6 hours at a flow rate of 0.50 L/h.

Ultrapure water was supplied to the ion exchange column for 5 minutes, and the water discharged from the ion exchange column was sampled. The ammonium ion concentration in the discharged water was measured, and found to be 770 mg/L.

Ultrapure water was supplied to the ion exchange column for 10 minutes, and the water discharged from the ion exchange column was sampled. The ammonium ion concentration in the discharged water was measured, and found to be 6.6 mg/L.

The ion conversion rate (%) (i.e., the rate of conversion into the carbonate form or the bicarbonate form) of the anion exchanger b was calculated in the same manner as in Example 1. The results are shown in Table 1.

[0130]

TABLE 1

	Example 1	Comparative Example 1	Comparative Example 2
R-OH form (eq%)	<0.1	<0.1	<0.1
R-CO ₃ form (eq%)	18.0	32.2	31.8
R-HCO ₃ form (eq%)	82.0	67.8	68.2

5 [0131]

Example 2

Hydrogen peroxide solution purification test

A hydrogen peroxide solution purification test was performed using the mixed bed A including the anion exchanger and the cation exchanger obtained in Example 1.

10 A 35 wt% hydrogen peroxide solution having a metal content of 10 ppb was used as the purification target sample. The hydrogen peroxide solution was passed through the mixed bed A for 4 hours in the downward direction at a temperature of 5°C and a flow rate of 0.5 L/h. The hydrogen peroxide solution that flowed out from the lower part of the packed column was collected, and the metal content was analyzed using an ICP-MS
15 method. The results are shown in Table 2.

[0132]

TABLE 2

	Concentration at outlet of ion exchange column (ppb)
Li	<0.01
Na	<0.01
Mg	<0.01
Al	<0.01
K	<0.01
Ca	<0.02
Cr	<0.01
Mn	<0.01
Fe	<0.01
Co	<0.01
Ni	<0.01
Cu	<0.01
Zn	<0.01
Cd	<0.01
Pb	<0.01

[0133]

5 Example 3

An ion exchange column made of PFA (copolymer of tetrafluoroethylene and perfluoroalkyl vinyl ether) (inner diameter: 16 mm, height: 30 cm) (see FIG. 1) was provided with a PFA mesh (at the bottom), and packed with 50 mL of a strongly basic type I anion-exchange resin (“ESG4002” manufactured by Organo Corporation, OH
10 form). Ultrapure water and carbon dioxide (controlled using a gas mass flow controller) were supplied to a gas dissolution hollow fiber membrane, and the carbon dioxide was dissolved in the ultrapure water to obtain a carbon dioxide aqueous solution. The carbon dioxide aqueous solution was supplied to the ion exchange column, and passed through the ESG4002 packed bed. The flow rate inside the ion exchange
15 column was set to 3.0 L/h, and the amount of carbon dioxide supplied to the hollow fiber membrane was adjusted so that the electrical conductivity at the inlet of the ion exchange column was 38 $\mu\text{S}/\text{cm}$. The carbon dioxide aqueous solution was continuously passed through the packed bed until the electrical conductivity at the outlet of the ion exchange column became equal to the electrical conductivity (38 $\mu\text{S}/\text{cm}$) at

the inlet of the ion exchange column (about 90 minutes) to obtain an anion-exchange resin A.

[0134]

In order to calculate the ion conversion rate (%) (i.e., the rate of conversion into carbonate form or bicarbonate form) of the anion-exchange resin A, a sodium nitrate aqueous solution was passed through the packed bed, and neutralization titration of the obtained solution was performed using sodium hydroxide (indicator: phenolphthalein-methyl red mixture). The results are shown in Table 3.

[0135]

TABLE 3

	Example 3
R-OH form (eq%)	<0.1
R-CO ₃ form (eq%)	19.8
R-HCO ₃ form (eq%)	80.2

[0136]

Example 4

An acetic acid aqueous solution was passed through an anion-exchange resin A prepared in the same manner as in Example 3 at a flow rate of 1.5L/h using a pump, and the acetic acid removal performance was determined. The acetic acid concentration at the inlet and the acetic acid concentration at the outlet were measured using a TOC analyzer ("Sievers 900" manufactured by GE). Note that the acetic acid concentration at the inlet was adjusted to 24.9 ppm. The results are shown in Table 3.

[0137]

Comparative Example 3

The acetic acid removal performance was determined in the same manner as in Example 4, except that an anion-exchange resin a prepared in the same manner as in Comparative Example 1 was used. The results are shown in Table 3.

The time elapsed until acetic acid broke was short (i.e., the treatment performance was low) as compared with Example 4.

[0138]

Example 5

5 Hydrogen peroxide solution purification test

A hydrogen peroxide solution purification test was performed using the anion-exchange resin A obtained in Example 3. A 35 wt% hydrogen peroxide solution including 10 ppb of Cr and Fe (that were present in the form of anions) was used as the purification target sample. The hydrogen peroxide solution was passed through the anion-exchange resin A for 4 hours in the downward direction at a temperature of 5°C and a flow rate of 0.5 L/h. The hydrogen peroxide solution that flowed out from the lower part of the packed column was collected, and the content of Cr and Fe was analyzed using an ICP-MS method. It was found that the content of Cr and Fe at the outlet was less than 0.01 ppb.

15

REFERENCE SIGNS LIST

[0139]

- 1 Ion exchange column made of PFA
- 2 Gas dissolution hollow fiber membrane
- 20 3 Gas mass flow controller
- 4 Carbon dioxide cylinder
- 5 Ultrapure water
- 6 Electrical conductivity meter
- 7, 8 Valve

25

CLAIMS

1. A method for producing an anion exchanger-cation exchanger mixture comprising an anion exchanger conversion step (1) that brings a carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water into contact with a mixture that comprises an anion exchanger (B) and a cation exchanger to convert the anion exchanger (B) into an anion exchanger (A) that comprises a bicarbonate form, or comprises a bicarbonate form and a carbonate form, to obtain a mixture that comprises the anion exchanger (A) and the cation exchanger.

2. The method for producing an anion exchanger-cation exchanger mixture according to claim 1, wherein the anion exchanger (A) is an anion exchanger in which a ratio of an exchange capacity of the bicarbonate form to a total exchange capacity of the bicarbonate form and the carbonate form is 70 eq% or more.

3. The method for producing an anion exchanger-cation exchanger mixture according to claim 1 or 2, wherein the anion exchanger conversion step (1) brings the carbon dioxide aqueous solution into contact with the mixture that comprises the anion exchanger (B) and the cation exchanger until a ratio of electrical conductivity of the carbon dioxide aqueous solution that has been brought into contact with the mixture that comprises the anion exchanger (B) and the cation exchanger to electrical conductivity of the carbon dioxide aqueous solution before being brought into contact with the mixture that comprises the anion exchanger (B) and the cation exchanger ((electrical conductivity after contact / electrical conductivity before contact) × 100)) reaches 90% or more.

4. A method for producing an anion exchanger-cation exchanger mixed bed

comprising an anion exchanger conversion step (2) that brings a carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water into contact with a mixed bed that is packed in an ion exchange column and comprises an anion exchanger (B) and a cation exchanger to convert the anion exchanger (B) into an anion exchanger (A) that comprises a bicarbonate form, or comprises a bicarbonate form and a carbonate form, to obtain a mixed bed that comprises the anion exchanger (A) and the cation exchanger.

5. The method for producing an anion exchanger-cation exchanger mixed bed according to claim 4, wherein the anion exchanger (A) is an anion exchanger in which a ratio of an exchange capacity of the bicarbonate form to a total exchange capacity of the bicarbonate form and the carbonate form is 70 eq% or more.

6. The method for producing an anion exchanger-cation exchanger mixed bed according to claim 4 or 5, wherein the anion exchanger conversion step (2) supplies the carbon dioxide aqueous solution to the ion exchange column until a ratio of electrical conductivity of the carbon dioxide aqueous solution at an outlet of the ion exchange column to electrical conductivity of the carbon dioxide aqueous solution at an inlet of the ion exchange column ((electrical conductivity at outlet / electrical conductivity at inlet) $\times$ 100)) reaches 90% or more.

7. A method for purifying a hydrogen peroxide solution comprising:
an anion exchanger conversion step (2) that brings a carbon dioxide aqueous solution obtained by dissolving carbon dioxide in purified water or ultrapure water into contact with a mixed bed that is packed in an ion exchange column and comprises an anion exchanger (B) and a cation exchanger to convert the anion exchanger (B) into an anion exchanger (A) that comprises a bicarbonate form, or comprises a bicarbonate

form and a carbonate form, to obtain a mixed bed that comprises the anion exchanger (A) and the cation exchanger; and

a hydrogen peroxide solution purification step that supplies a crude hydrogen peroxide solution to the ion exchange column so that the crude hydrogen peroxide solution is brought into contact with the mixed bed that comprises the anion exchanger (A) and the cation exchanger to obtain a purified hydrogen peroxide solution.

8. The method for purifying a hydrogen peroxide solution according to claim 7, wherein the anion exchanger conversion step (2) supplies the carbon dioxide aqueous solution to the ion exchange column until a ratio of electrical conductivity of the carbon dioxide aqueous solution at an outlet of the ion exchange column to electrical conductivity of the carbon dioxide aqueous solution at an inlet of the ion exchange column $((\text{electrical conductivity at outlet} / \text{electrical conductivity at inlet}) \times 100)$ reaches 90% or more.