

DESCRIPTION

Deionized Water Manufacturing System, Electrodeionization Device,
and Method for Manufacturing Deionized Water

TECHNICAL FIELD

[0001]

The present invention relates to the manufacture of deionized water, and more particularly relates to a deionized water manufacturing system, an electrodeionization device, and a method for manufacturing deionized water.

BACKGROUND ART

[0002]

Deionized water manufacturing systems are known that carry out deionization by means of an ion exchange reaction in which water to be processed is passed through an ion exchanger such as an ion exchange resin. This type of system is typically provided with a device having an ion exchanger and produces deionized water by using an ion exchange reaction realized by the ion exchanger. In a device having an ion exchanger, however, when the ion exchange group of the ion exchanger becomes saturated and the deionization performance declines, a process of regenerating the ion exchanger by means of a chemical such as an acid or alkali, *i.e.*, a regeneration process, must be carried out. The regeneration process replaces the cations (positive ions) and anions (negative ions) that have been adsorbed on the ion exchanger with hydrogen ions (H^+) and hydroxide ions (OH^-) that originate in acid or alkali and is thus a process of restoring the deionization performance of the ion exchanger. Accordingly, a deionized water manufacturing device that uses an ion exchanger entails the problem that time and effort must be taken for chemical replenishment for a regeneration process and continuous operation therefore

cannot be carried out. As a means for solving this problem, recent years have seen the development and practical application of electric deionized water manufacturing devices (also referred to as EDI (ElectroDeionization) devices) that do not require regeneration by chemicals.

[0003]

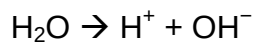
An EDI device is a device in which electrophoresis and electrodialysis are combined and has a construction in which an ion exchanger is packed between an anion exchange membrane that allows permeation of only anions and a cation exchange membrane that allows permeation of only cations to form a deionization chamber, concentration chambers being respectively arranged outside the anion exchange membrane and cation exchange membrane as seen from the deionization chamber, and further, an anode chamber that is provided with an anode and a cathode chamber that is provided with a cathode being arranged outside of these concentration chambers. The ion exchanger that is packed in the deionization chamber is at least one of an anion exchanger and cation exchanger. In the deionization chamber, the anion exchange membrane is arranged on the side that faces the anode, and the cation exchange membrane is arranged on the side that faces the cathode. An ion exchanger may also be packed in the concentration chambers, a cation exchanger may be packed in the anode chamber, and an anion exchanger may be packed in the cathode chamber.

[0004]

To manufacture deionized water by an EDI device from the water that is to be processed, the water to be processed is fed to the deionization chamber in a state in which a dc voltage is applied between the anode and cathode. The ion components in the water to be processed are thereupon adsorbed to the ion exchanger in the deionization chamber whereby a deionization process, *i.e.*, a

desalination process, is carried out. As a result, deionized water flows from the deionization chamber. In the deionization chamber at this time, a disassociation reaction of water occurs at the interfaces between the different types of ion exchange substances, *i.e.*, the interface between the anion exchanger and cation exchanger, the interface between the anion exchanger and the cation exchange membrane, the interface between the anion exchange membrane and the cation exchanger, and the interface between the anion exchange membrane and the cation exchange membrane, due to the application of voltage as shown in the formula shown below, hydrogen ions and hydroxide ion being generated as a result.

[0005]



Due to the hydrogen ions and hydroxide ions that are generated by this disassociation reaction, the ion components that have been previously adsorbed to the ion exchanger in the deionization chamber undergo ion exchange and are freed from the ion exchanger. The anions among the freed ion components undergo electrophoresis as far as the anion exchange membrane and then undergo electro dialysis in the anion exchange membrane and are discharged into concentrated water flowing through the concentration chamber that is closer to the anode as seen from the deionization chamber. Similarly, of the freed ion components, the cations undergo electrophoresis as far as the cation exchange membrane, undergo electro dialysis at the cation exchange membrane, and are discharged into concentrated water flowing through the concentration chamber that is closer to the cathode as seen from deionization chamber. In the end, the ion components in the water to be processed that is supplied to the deionization chamber migrate to the concentration chambers and are discharged, while at the same time, the ion exchanger of the deionization chamber is regenerated.

[0006]

Thus, in an EDI device, the hydrogen ions and hydroxide ions that are generated by the application of a dc voltage continuously act as the acid and alkali regeneration agents that regenerate the ion exchanger. As a result, in the EDI device, the regeneration process by means of chemicals supplied from the outside becomes basically unnecessary and continuous operation can be carried out without performing the regeneration of the ion exchangers by means of chemicals.

[0007]

In the foregoing explanation, a basic configuration composed of [concentration chamber (C) | anion exchange membrane (AEM) | deionization chamber (D) | cation exchange membrane (CEM) | concentration chamber (C)] is assumed to be arranged between the anode and the cathode. This basic configuration is referred to as a cell set. In actuality, it is typical to juxtapose a plurality of cell sets of this type between the electrodes and electrically connect the plurality of cell sets in series with one end as the anode and the other end as the cathode to realize a large increase in processing capability. Because neighboring concentration chambers can be shared between adjacent cell sets in this case, the configuration of an EDI device becomes: [anode chamber | C | AEM | D | CEM | C | AEM | D | CEM | C | AEM | D | CEM | ... | C | cathode chamber]. In addition, a cation exchange membrane is usually provided between the anode chamber and the adjacent concentration chamber, and an anion exchange membrane is usually provided between the cathode chamber and the adjacent concentration chamber. Further, in a serial configuration of this type, regarding the deionization chamber that is closest to the anode chamber, the anode chamber itself can also be caused to function as a concentration chamber without interposing an independent concentration

chamber between the anode chamber and the deionization chamber. Similarly, regarding the deionization chamber that is closest to the cathode chamber, the cathode chamber itself can also be caused to function as a concentration chamber without interposing a concentration chamber between the cathode chamber and the deionization chamber. An ion exchanger is also preferably packed in each concentration chamber, anode chamber, and cathode chamber to lower the electrical resistance in order to suppress the electric power that is consumed by the application of the dc voltage.

[0008]

In a deionized water manufacturing system provided with an EDI device, water in which impurities have to some extent been reduced in advance is preferably used as the water to be processed that is supplied to the EDI device in order to obtain deionized water having extremely low concentration of impurities. As a result, the deionized water manufacturing system is configured by providing, for example, a reverse-osmosis (RO) membrane device in the stage preceding the EDI device, and water that has passed through the reverse-osmosis membrane device is supplied to the EDI device as the water to be processed. However, the electric conductivity of the water to be processed is reduced, and when the conductivity falls to, for example, 5 $\mu\text{S}/\text{cm}$ or below, the voltage that must be applied to the EDI device in order to bring about the disassociation reaction of the water becomes high. When water to be processed having lower conductivity is used to obtain deionized water in which the concentration of impurities is even lower, the voltage that must be applied to the EDI device, *i.e.*, the operating voltage, becomes higher if the current that flows between the anode and cathode is assumed to be fixed. If the operating voltage becomes higher, the power consumption increases proportionally.

[0009]

As described hereinabove, the disassociation reaction of water inside the deionization chamber plays a crucial role in the continuous manufacture of deionized water by means of an EDI device. If the disassociation reaction of water is carried out efficiently, the voltage applied to the EDI device can be suppressed to a low level even when the conductivity of the water to be processed is low, and as a result, high-purity deionized water can be manufactured with low power consumption.

[0010]

A number of techniques have been proposed for promoting the disassociation reaction of water inside the deionization chamber of an EDI device. Patent Literature 1 discloses having the membrane surface on the deionization chamber-side of the cation exchange membrane or the ion exchange resin packed inside the deionization chamber in an EDI device support a metal hydroxide such as magnesium hydroxide. Patent Literature 2 discloses the mixing of a metal oxide or metal hydroxide that acts as an amphoteric ion exchanger in an ion exchanger inside the deionization chamber at a proportion of volume ratio of from 1 to 50% in an EDI device.

CITATION LIST

Patent Literatures

[0011]

Patent Literature 1: JP 2000-350991 A1

Patent Literature 2: JP 2001-340865 A2

SUMMARY OF THE INVENTION

Technical Problem

[0012]

In the device disclosed in Patent Literature 1, however, the metal hydroxide supported within the deionization chamber is dissolved by the

hydrogen ions that are generated by the disassociation of water, and it is therefore difficult to stabilize and maintain performance over a long time interval. In the device described in Patent Literature 2, the metal oxides and metal hydroxides that have been mixed in the ion exchanger are not reliably present at the interfaces of the different types of ion exchangers, whereby the effect of promoting water disassociation cannot be exhibited to the maximum.

[0013]

In consideration of the problems of the deionized water manufacturing systems of the prior art as described above, it is an object of the present invention to provide a deionized water manufacturing system and deionized water manufacturing method that promote a more stable and efficient disassociation reaction of water to enable the manufacture of high-purity deionized water at low power consumption, even when the water to be processed having low conductivity is supplied to the electrodeionization device, as well as an electrodeionization device that is suitable for use in the deionized water manufacturing system.

[0014]

It is another object of the present invention to provide at least one of an ion exchange membrane and an ion exchanger that are used in the electrodeionization device.

Solution to Problem

[0015]

According to one aspect of the present invention, a deionized water manufacturing system that is supplied with raw water and that manufactures deionized water is provided with: a reverse-osmosis membrane device to which raw water is supplied, and an electrodeionization device that includes a deionization chamber which is partitioned by an ion exchange membrane and to

which permeated water of the reverse-osmosis membrane device is supplied, wherein an ion exchanger is packed inside the deionization chamber, and wherein particles containing polyvalent metal are adsorbed to at least one surface of at least one portion of the ion exchange membrane and at least one portion of the ion exchanger.

[0016]

According to another aspect of the present invention, an electrodeionization device (EDI device) that is equipped with at least one deionization chamber between an anode chamber that is provided with an anode and a cathode chamber that is provided with a cathode, the deionization chamber being partitioned by an anion exchange membrane that is positioned on a side facing the anode and a cation exchange membrane that is positioned on a side facing the cathode, and at least one of an anion exchanger and a cation exchanger being packed inside the deionization chamber, is characterized in that particles containing polyvalent metal are adsorbed to at least one surface of the anion exchange membrane, the cation exchange membrane, the anion exchanger, and the cation exchanger.

[0017]

The polyvalent metal, *i.e.*, metallic elements in which the ionic valence upon becoming cations is two or more, acts as a catalyst of the disassociation reaction of water. In the present invention, particles containing polyvalent metal are adsorbed to the surface of at least one of the anion exchanger, cation exchanger, anion exchange membrane, and cation exchange membrane inside the deionization chamber, thereby reliably ensuring the existence of polyvalent metal that acts as the catalyst of the water disassociation reaction at the interfaces between different types of ion exchange substances inside the deionization chamber. As a result, the maximum effect of promoting the water

disassociation reaction by the polyvalent metal can be obtained in the present invention. In addition, the particles that contain polyvalent metal have the shape of particles, whereby, when being adsorbed to the ion exchanger and ion exchange membranes inside the deionization chamber, the concern that these surfaces will be covered with the particles containing polyvalent metal is eliminated and the loss of permeability of the ions and the reactivity of the ion exchange relating to deionization can therefore be suppressed to a minimum.

[0018]

According to yet another aspect of the present invention, a deionized water manufacturing method is characterized in that, in a deionized water manufacturing method that uses the above-described EDI device of the present invention, deionized water is obtained by causing water that is to be processed to flow through the deionization chamber while applying a dc voltage between the anode and cathode such that the current density in the deionization chamber is at least 0.3 A/dm^2 but no greater than 10 A/dm^2 .

[0019]

According to another aspect of the present invention, in a deionized water manufacturing method that uses an EDI device which is equipped with at least one deionization chamber between an anode chamber that is provided with an anode and a cathode chamber that is provided with a cathode and in which the deionization chamber is partitioned by an anion exchange membrane that is positioned on the side facing the anode and a cation exchange membrane that is positioned on the side facing the cathode, at least one of anion exchanger and cation exchanger being packed inside the deionization chamber; a deionized water manufacturing method includes steps of: causing particles that contain polyvalent metal to be adsorbed to the surface of at least one of an anion exchange membrane, a cation exchange membrane, an anion exchanger, and a

cation exchanger; and after the step of adsorbing, obtaining deionized water by causing water that is to be processed to flow through the deionization chamber while applying a dc voltage between the anode and the cathode.

[0020]

According to yet another aspect of the present invention, in an ion exchange membrane that is used in an EDI device that is equipped with at least one deionization chamber between an anode chamber that is provided with an anode and a cathode chamber that is provided with a cathode, the deionization chamber being packed with at least one of anion exchanger and cation exchanger, an ion exchange membrane for EDI device is characterized in that particles that contain polyvalent metal are caused to be adsorbed to a surface of an ion exchange membrane, the ion exchange membrane being at least one of: an anion exchange membrane that partitions the deionization chamber and that is positioned on the side facing the anode in the deionization chamber; a cation exchange membrane that partitions the deionization chamber and that is positioned on the side facing the cathode in the deionization chamber; and an intermediate ion exchange membrane that further partitions the inside of the deionization chamber into small deionization chambers.

[0021]

According to yet another aspect of the present invention, in an ion exchanger that is used in an EDI device that is equipped with at least one deionization chamber between an anode chamber that is provided with an anode and a cathode chamber that is provided with a cathode, the deionization chamber being partitioned by an anion exchange membrane that is positioned on the side facing the anode and a cation exchange membrane that is positioned on the side facing the cathode, an ion exchanger for EDI device which is at least one of anion exchanger and cation exchanger and is packed

inside the deionization chamber is characterized in that particles that contain polyvalent metal are caused to be adsorbed into the surface of the ion exchanger.

[0022]

As will become clear from the Examples and so on to be described hereinbelow, according to the present invention, causing particles that contain polyvalent metal to be adsorbed to an ion exchanger or ion exchange membrane inside a deionization chamber of an EDI device enables the promotion of a more stable and efficient disassociation reaction of water compared to an EDI device in which particles that contain polyvalent metal are not used, and as a result, high-purity deionized water can be manufactured with lower consumption of electric power.

BRIEF DESCRIPTION OF DRAWINGS

[0023]

FIG. 1 shows the configuration of a deionized water manufacturing system based on the present invention.

FIG. 2 shows another example of the configuration of the deionized water manufacturing system.

FIG. 3 shows yet another example of the configuration of the deionized water manufacturing system.

FIG. 4 is a schematic sectional view that shows the basic embodiment of an electrodeionization device (EDI device).

FIG. 5A is a view for describing the promotion of the water disassociation realized by particles that contain polyvalent metal.

FIG. 5B is a view for describing the promotion of the water disassociation realized by particles that contain polyvalent metal.

FIG. 6 is a schematic sectional view showing another embodiment of the

EDI device based on the present invention.

FIG. 7 is a schematic sectional view showing yet another embodiment of the EDI device based on the present invention.

FIG. 8 is a schematic sectional view showing yet another embodiment of the EDI device based on the present invention.

FIG. 9 is a schematic sectional view showing yet another embodiment of the EDI device based on the present invention.

FIG. 10 is a schematic sectional view showing yet another embodiment of the EDI device based on the present invention.

FIG. 11 is a view for describing the promotion of the water disassociation realized by particles that contain polyvalent metal.

FIG. 12 is a schematic sectional view showing yet another embodiment of the EDI device based on the present invention.

FIG. 13 is a schematic sectional view showing yet another embodiment of the EDI device based on the present invention.

DESCRIPTION OF EMBODIMENT

[0024]

Preferable exemplary embodiments of the present invention are next described with reference to the accompanying drawings.

[0025]

FIG. 1 shows the configuration of a deionized water manufacturing system that is based on the present invention. This deionized water manufacturing system is a device that is equipped with EDI device 10, and in order to obtain deionized water in which the concentration of impurities is sufficiently reduced, reverse-osmosis (RO) membrane devices 51 and 52 are provided in a two-pass series in the stage preceding EDI device 10. Reverse-osmosis membrane devices 51 and 52 are equipped with reverse-osmosis

membranes 53 and 54 inside these devices, respectively. First-pass reverse-osmosis membrane device 51 is supplied with raw water by way of pump 55, and the water that has passed through reverse-osmosis membrane 53 inside reverse-osmosis membrane device 51, *i.e.*, permeated water, is supplied to second-pass reverse-osmosis membrane device 52. The permeated water of second-pass reverse-osmosis membrane device 52 is supplied to EDI device 10 as water to be processed. The configuration in which two reverse-osmosis membrane devices 51 and 52 are connected in a series is a configuration in which, overall, devices that are equipped with respective reverse-osmosis membranes 53 and 54 are connected in a two-pass series. Reverse-osmosis membrane devices 51 and 52 used in the deionized water manufacturing system of the present exemplary embodiment are typical devices used in, for example, the manufacture of pure water. In addition, a configuration may also be adopted in which tanks and pumps, ion exchange resin devices for the purpose of softening or deionization, a decarbonator or membrane degasification device for the purpose of decarbonation, and further, chemical injection equipment, and so on may be suitably added and arranged as necessary among pump 55, reverse-osmosis membrane devices 51 and 52, and EDI device 10 shown in the figure.

[0026]

Tap water, well water, river water, or water for industrial purposes is used as the raw water. Supply water is supplied to EDI device 10 other than the water to be processed as will be described hereinbelow. Supply water may be permeated water obtained from, for example, a reverse-osmosis membrane device, or may be water that has been processed by an EDI device, *i.e.*, deionized water. In this case, two reverse-osmosis membrane devices 51 and 52 are provided, but as shown in FIG. 2, only single-pass reverse-osmosis

membrane device 52 may be provided in the stage preceding EDI device 10.

[0027]

The EDI devices may be connected in a two-pass series in order to obtain deionized water in which the concentration of impurities has been even further reduced than in the system shown in FIG. 1. FIG. 3 shows a device in which additional EDI device 15 has been arranged between reverse-osmosis membrane device 52 and EDI device 10 in the deionized water manufacturing system shown in FIG. 1. As EDI device 15, a device having the same configuration as EDI device 10 can be used, or a device having a different configuration can be used. The permeated water of reverse-osmosis membrane device 52 is supplied to deionization chamber 23 of EDI device 15, and the water that flows from deionization chamber 23 of EDI device 15 is supplied to the deionization chamber of EDI device 10 as the water to be processed. In addition, tanks and pumps, ion exchange resin devices for the purpose of softening or deionization, a decarbonator or membrane degasification device for the purpose of decarbonation, as well as chemical injection equipment may also be added as appropriate and arranged among pump 55, reverse-osmosis membrane devices 51 and 52, and EDI devices 10 and 15 shown in the figure.

[0028]

In the case of the configuration shown in FIG. 3, the conductivity of the water to be processed that is supplied to the second-pass EDI device 10 is already an extremely low value of, for example, 1 $\mu\text{S}/\text{cm}$ or lower. When an EDI device is used to manufacture deionized water, the operating voltage of the EDI device tends to become higher in cases in which the conductivity of the water to be processed is low, but the use of the EDI device described later that is based on the present invention as later-pass EDI device 10 allows the operating voltage of this EDI device 10 to remain low. The conductivity of the water to be

processed that is supplied to the first-pass additional EDI device 15 is relatively great, and as a result, rather than the EDI device that is described later, a typical EDI device can be used as additional EDI device 15.

[0029]

In each of the deionized water manufacturing systems shown in FIGs. 1, 2, and 3, the conductivity of the water to be processed for EDI device 10 is, for example, no greater than 10 $\mu\text{S}/\text{cm}$, preferably no greater than 5 $\mu\text{S}/\text{cm}$, more preferably no greater than 3 $\mu\text{S}/\text{cm}$, and still more preferably no greater than 1 $\mu\text{S}/\text{cm}$.

[0030]

Explanation next regards EDI device 10 that is based on the present invention and that is used in the above-described deionized water manufacturing system. In EDI device 10, concentration chamber 22, deionization chamber 23, and concentration chamber 24 are provided in that order from the side of anode chamber 21 between anode chamber 21 that is provided with anode 11 and cathode chamber 25 that is provided with cathode 12. Anode chamber 21 and concentration chamber 22 are adjacent with cation exchange membrane 31 interposed. Concentration chamber 22 and deionization chamber 23 are adjacent with anion exchange membrane 32 interposed. Deionization chamber 23 and concentration chamber 24 are adjacent with cation exchange membrane 33 interposed. Concentration chamber 24 and cathode chamber 25 are adjacent with anion exchange membrane 34 interposed. Accordingly, deionization chamber 23 is partitioned by anion exchange membrane 32 that is positioned on the side facing anode 11 and cation exchange membrane 33 that is positioned on the side facing cathode 12. At least one of an anion exchanger and a cation exchanger is packed inside deionization chamber 23. In the example shown here, an anion exchanger and a cation exchanger are packed

inside deionization chamber 23 in a mutually mixed configuration, *i.e.*, a mixed-bed configuration. Further, in this EDI device 10, a cation exchanger is packed inside anode chamber 21 and an anion exchanger is packed inside concentration chambers 22 and 24 and cathode chamber 25. In this case, for example, an anion exchange resin is used as the anion exchanger and, for example, a cation exchange resin is used as the cation exchanger. In addition, an anion exchanger or a cation exchanger is not necessarily packed in anode chamber 21, concentration chambers 22 and 24, and cathode chamber 25. FIG. 4 gives a schematic representation of the sectional configuration of EDI device 10 that is used in the deionized water manufacturing system shown in FIG. 1. In FIG. 4, the small circles drawn inside electrode chambers 21 and 25, concentration chambers 22 and 24, and deionization chamber 23 show the anion exchangers and cation exchangers that are packed inside these chambers. In addition, although mutually identical hatching is added to the anion exchanger and anion exchange membrane, and mutually identical hatching is added to the cation exchanger and cation exchange membrane in FIG. 4, the anion exchanger and cation exchanger are depicted by distinguishing them by the addition of different hatching. The distinction between the anion exchanger and cation exchanger and the distinction between the anion exchange membrane and cation exchange membrane realized by the hatching are common to each of the drawings appended to the present Description.

[0031]

In the following explanation, the anion exchanger and cation exchanger are referred to by the general term "ion exchanger," and the anion exchange membrane and cation exchange membrane are referred to by the general term "ion exchange membrane." Accordingly, an ion exchanger is at least one of an

anion exchanger and cation exchanger, and an ion exchange membrane is at least one of an anion exchange membrane and a cation exchange membrane. [0032]

Still further, in deionization chamber 23 in this EDI device 10, particles that contain polyvalent metal are adsorbed to at least one of the surfaces of at least a portion of the ion exchangers that are provided in deionization chamber 23 and at least a portion of ion exchange membranes (anion exchange membrane 32 and cation exchange membrane 33). The “particles that contain polyvalent metal” referred to here are particles that contain polyvalent metal, *i.e.*, a metal element for which the ionic valency is at least “2” upon becoming a cation, are adsorbed to an anion exchanger, cation exchanger, anion exchange membrane, or cation exchange membrane, and moreover, do not easily mechanically separate after having been adsorbed. No particular limitations apply to the material that is here used as the polyvalent metal as long as the material acts as a catalyst of water disassociation, and further, the material may be a single type of metal or may contain a plurality of types of metal. Examples of the metal element that is used as the polyvalent metal include magnesium, calcium, aluminum, chromium, manganese, iron, nickel and so on. Thus, “particles that contain polyvalent metal” can be considered to be a material that acts as a catalyst of water disassociation and “particles that contain polyvalent metal” are therefore hereinbelow referred to as simply “catalyst particles” unless stated otherwise.

[0033]

No particular limitations apply to the catalyst particles as long as they are easily adsorbed to the surface of an anion exchanger, cation exchanger, anion exchange membrane, or cation exchange membrane. When the catalyst particles are an inorganic substance, the catalyst particles are preferably an

inorganic ion exchange material from the viewpoint of ease of adsorption. An inorganic ion exchange material is an inorganic substance having the capability of carrying out exchange of ion species by taking in ions contained in an electrolytic solution that is in contact, and in exchange, releasing ions belonging to itself, or in other words, an inorganic substance having an ion exchange capacity. The reason that catalyst particles that are an inorganic ion exchange material are easily adsorbed to the surface of an anion exchanger, cation exchanger, anion exchange membrane, or cation exchange membrane is presumed to be because the catalyst particles adsorb to the surface of the anion exchanger, cation exchanger, anion exchange membrane or cation exchange membrane by way of ion exchange groups that are present on these surfaces. [0034]

Silicate that contains polyvalent metal can be preferably used as an example of catalyst particles that are an inorganic ion exchange material, and examples of this type of silicate include aluminum silicate, magnesium silicate, calcium silicate, calcium-magnesium silicate, various types of aluminosilicate, and various types of silicate minerals; and one or more from among these materials can also be used independently or mixed together. Of these, a silicate mineral has superior chemical stability, and in particular, strongly adsorbs to an anion exchanger or anion exchange membrane, and therefore can be expected to exhibit more stable performance. Further, a silicate mineral is contained in natural ore and therefore has more options and is advantageous from the viewpoint of cost. Examples of such a silicate mineral include: zeolite, talc, kaolinite, and zeolite, and in particular, sepiolite (CAS number (Chemical Abstract Service registry number): 63800-37-3, composition formula: $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot 8\text{H}_2\text{O}$), wollastonite (CAS number: 13983-17-0, composition formula: CaSiO_3), and attapulgite (CAS number: 12174-11-7,

composition formula: $(\text{Mg}, \text{Al})_5\text{Si}_8\text{O}_{20} \cdot 4\text{H}_2\text{O}$) have high adsorptive properties and are therefore more suitably used. A material composed of at least one of attapulgite, sepiolite, and wollastonite is more preferably used as the catalyst particles. Attapulgite, sepiolite, and wollastonite are further known to be in the form of acicular particles. The ease with which silicate minerals adsorb to, for example, an anion exchanger is presumed to be due to the electrostatic attraction of anion exchange groups such as amino groups or quaternary ammonium groups contained in an anion exchanger to, for example, hydroxy groups or oxygen atoms that are present on the surfaces of silicate minerals.

[0035]

The adsorption of catalyst particles to an ion exchanger or ion exchange membrane can be easily carried out by, for example, immersing an ion exchanger or ion exchange membrane in water in which catalyst particles have been dispersed. In addition, catalyst particles can be caused to adsorb to an ion exchanger or ion exchange membrane inside a deionization chamber of an existing EDI device by supplying water in which catalyst particles have been dispersed to the deionization chamber. Accordingly, an existing EDI device can be easily converted to an EDI device that is based on the present invention, and the manufacture of deionized water that follows conversion of an existing EDI device to an EDI device based on the present invention is included in the categories of the present invention.

[0036]

No particular limitation applies to the particle diameter of the catalyst particles. The particle diameter of each individual catalyst particle can be found by, for example, measurement in images obtained by observing the catalyst particles at a magnification on the order of 1000 to 20000 times by means of a scanning electron microscope (SEM). When the shape of the catalyst particles

is not spherical, the maximum diameter is taken as the particle diameter. For example, when the catalyst particles are acicular particles, the length along the longitudinal axis is taken as the particle diameter. The range of the particle diameter of the catalyst particles is the range from a minimum value to a maximum value of the measured particle diameters when the particle diameters of catalyst particles were measured in SEM images of ten sites having different observation fields. In the present invention, the use of catalyst particles for which the range of the particle diameter is, for example, at least 0.01 μm but no greater than 100 μm is preferable, and the use of catalyst particles for which the range is at least 0.02 μm but no greater than 10 μm is more preferable.

[0037]

When the particle size of catalyst particles is too great, not only are suitable adsorption and securement to the surfaces of the ion exchanger or ion exchange membrane prevented, but the distance between the interfaces of the different types of ion exchange substances becomes excessive, whereby the possibility arises that the water disassociation reaction cannot be adequately promoted. On the other hand, when the particle diameter of the catalyst particles is too small, the catalyst particles densely cover the surfaces of the ion exchanger or ion exchange membrane and therefore may bring about such problems as interference with the ion exchange reaction or ion migration on the ion exchanger or the ion exchange membrane.

[0038]

The ion exchanger that is packed in deionization chamber 23 is next described. No particular limitations apply to the type of ion exchanger that can be packed in deionization chamber 23, but as exemplified above, an ion exchange resin is preferable. An ion exchange resin described here is synthetic resin into which a functional group with an ion exchange capability, *i.e.*, an ion

exchange group, has been introduced into a polymer matrix having a three-dimensional reticulated structure. An ion exchange resin that is normally used has spherical particles for which the particle diameter is on the order of 0.4 to 0.8 mm. The polymer matrix of the ion exchange resin may be, for example, a styrene-divinylbenzene copolymer that is referred to as “styrene” or an acrylate-divinylbenzene copolymer referred to as “acrylic.”

[0039]

The ion exchange resins can be broadly divided between cation exchange resins in which the ion exchange group exhibits acidity and anion exchange resins in which the ion exchange group exhibits basicity, and further, can be divided into strongly acidic cation exchange resins, weakly acidic cation exchange resins, strongly basic anion exchange resins, weakly basic anion exchange resins and so on according to the type of ion exchange group that is introduced. Strongly basic anion exchange resins include, for example, resins that have a quaternary ammonium group as an ion exchange group, and weakly basic anion exchange resins include, for example, resins that have a primary amine, a secondary amine, or a tertiary amine as an ion exchange group. Strongly acidic cation exchange resins include, for example, resins that contain a sulfonic group as an ion exchange group, and weakly acidic cation exchange resins include, for example, resins that contain a carboxyl group as an ion exchange group. As the ion exchange resin packed in the deionization chamber, a substance of the any of these types can be used, but the combination of an ion exchange resin and catalyst particles in which catalyst particles are adsorbed to the ion exchange group contained by the ion exchange resin is preferably selected.

[0040]

The amount of adsorption of catalyst particles to the ion exchanger inside

deionization chamber 23 is at least 0.0001% by volume if represented by the volume ratio where the volume of the ion exchanger is 100%, and preferably less than 1 volume %, and more preferably no greater than 0.0125 volume %. If the amount of adsorption of catalyst particles is made excessively large, the catalyst particles may impede the ion exchange reaction or the ion migration inside EDI device 10.

[0041]

The manufacture of deionized water by means of EDI device 10 shown in FIG. 4 is next described.

[0042]

As with an EDI device of the prior art, supply water is fed to anode chamber 21, concentration chambers 22 and 24, and cathode chamber 25, and the water to be processed is passed to deionization chamber 23 in a state in which a dc voltage is applied between anode 11 and cathode 12. When water to be processed is supplied to deionization chamber 23, the ion components in the water to be processed are adsorbed to the ion exchanger in deionization chamber 23, the deionization process is carried out, and the deionized water flows out from deionization chamber 23 as processed water. In deionization chamber 23 at this time, a water disassociation reaction occurs at the interfaces between the different types of ion exchange substances due to the application of voltage, hydrogen ions and hydroxide ions are generated, and the ion components that have been earlier adsorbed to the ion exchangers in deionization chamber 23 undergo ion exchange to be freed from the ion exchangers due to the hydrogen ions and hydroxide ions. Of the ion components that are released, the anions move to concentration chamber 22 that is closer to the anode by way of anion exchange membrane 32 and are discharged from this concentration chamber 22 as concentrated water, and the

cations move to concentration chamber 24 that is closer to the cathode by way of cation exchange membrane 33 and are discharged as concentrated water from this concentration chamber 24. In the end, the ion components in the water to be processed that is supplied to deionization chamber 23 move to concentration chambers 22 and 24 and are discharged, while simultaneously, the ion exchangers in deionization chamber 23 are also regenerated. Further, electrode water is discharged from anode chamber 21 and cathode chamber 25.

[0043]

In EDI device 10 shown in FIG. 4, as described hereinabove, particles that contain polyvalent metal, *i.e.*, catalyst particles, are adsorbed to the surfaces of at least one of ion exchangers, anion exchange membrane 32, and cation exchange membrane 33 that are provided in deionization chamber 23. These catalyst particles are present at the interfaces of different types of ion exchange substances inside deionization chamber 23, but because the polyvalent metal contained in the catalyst particles acts as a catalyst that promotes the disassociation reaction of water, the disassociation reaction of water can be carried out efficiently in this EDI device 10. Accordingly, the regeneration of ion exchangers inside deionization chamber 23 can also be carried out efficiently, and high-purity deionized water can be manufactured at low power while suppressing the voltage that is applied to EDI device 10. In addition, to the extent that the applied voltage can be reduced, device operation becomes possible at a high current density in deionization chamber 23, for example, a current density of 0.3 A/dm^2 or more but no greater than 10 A/dm^2 .

[0044]

FIGs. 5A and 5B give schematic representations of the disassociation reaction of water by catalyst particles. It is here assumed that catalyst particles 43 are adsorbed to anion exchanger 42. When the interfaces of different types

of ion exchange substances are made up by cation exchanger 41 and anion exchanger 42, the disassociation of water at these interfaces is promoted and the hydroxide ions are efficiently generated on the anion exchanger 42 side and hydrogen ions are efficiently generated on the cation exchanger 41 side, as shown in FIG. 5A. Similarly, at the interface of anion exchanger 42 and cation exchange membrane 33, hydroxide ions are efficiently generated on the anion exchanger 42 side and hydrogen ions are efficiently generated on the cation exchange membrane 33 side, as shown in FIG. 5B. This EDI device 10 enables the promotion of the disassociation of water at the interfaces of the ion exchange membranes and ion exchangers.

[0045]

Although the basic configuration of EDI device 10 based on the present invention has been described above, the present invention can also be widely applied to EDI devices of various configurations. Examples of the configuration of an EDI device to which the present invention can be applied are described below. In any case, particles that contain polyvalent metal, *i.e.*, catalyst particles, are adsorbed to the ion exchanger or ion exchange membrane in at least deionization chamber 23. The EDI devices that are described below are devices that can be used as EDI device 10 in the deionized water manufacturing system shown in any of FIGs. 1, 2, and 3.

[0046]

FIG. 6 shows another embodiment of the EDI device based on the present invention. As described above, in an EDI device, a plurality of basic configurations (*i.e.*, cell sets) made up from [concentration chamber | anion exchange membrane (AEM) | deionization chamber | cation exchange membrane (CEM) | concentration chamber] can be arranged juxtaposed between the anode and the cathode. At this time, concentration chambers that

adjoin each other between adjacent cell sets can be shared. The EDI device shown in FIG. 6 is a construction in which a plurality of cell sets are arranged in this way in the device shown in FIG. 4, and, as a construction in which one cell set is made up from anion exchange membrane 32, deionization chamber 23, cation exchange membrane 33, and concentration chamber 24, a number N of these cell sets are arranged between concentration chamber 22 that is closest to anode chamber 21 and cathode chamber 25. Here, N is an integer equal to or greater than 1. Cation exchange resin (CER) is packed in anode chamber 21, and anion exchange resin (AER) is packed in concentration chambers 22 and 24 and cathode chamber 25. Anion exchange resin and cation exchange resin are packed in deionization chamber 23 in a mixed bed (MB) configuration. Instead of water being supplied to anode chamber 21 from the outside, the output water of cathode chamber 25 is supplied to anode chamber 21. In contrast to the construction shown in FIG. 4, the direction of the flow of water inside deionization chamber 23 is a countercurrent with respect to the direction of flow of water in concentration chambers 22 and 24 on both sides of deionization chamber 23.

[0047]

FIG. 7 shows another embodiment of an EDI device based on the present invention. This EDI device is similar to that of the device shown in FIG. 4, but, inside deionization chamber 23, an anion exchange resin is arranged in the region close to the inlet of water to be processed, and an anion exchange resin and cation exchange resin are provided as a mixed bed in the region close to the outlet. As a matter of course, with one cell set being made up by anion exchange membrane 32, deionization chamber 23, cation exchange membrane 33, and concentration chamber 24, a number N of the cell sets can be arranged between concentration chamber 22 that is closest to anode chamber 21 and

cathode chamber 25. Here, N is an integer equal to or greater than 1.

[0048]

The EDI device shown in FIG. 8 has a construction similar to the EDI device shown in FIG. 7, but deionization chamber 23 is divided into four regions along the direction of water flow in the deionization chamber, and ion exchange resins are arranged in each region such that a cation exchange resin, anion exchange resin, cation exchange resin, and anion exchange resin are aligned in order from the position of the inlet of water to be processed. In other words, the EDI device shown in FIG. 8 is of a configuration provided with, in deionization chamber 23, ion exchangers in a multilayered bed configuration in which cation exchange resin layers and anion exchange resin layers are alternately arranged along the direction of flow of the water. In the EDI device shown in FIG. 8, moreover, in contrast to the configuration shown in FIG. 7, the direction of flow of water inside deionization chamber 23 is a countercurrent with respect to the direction of flow of water in concentration chambers 22 and 24 on both sides of deionization chamber 23.

[0049]

The EDI device shown in FIG. 9 is similar to device shown in FIG. 7, but deionization chamber 23 is divided into three regions along the direction of flow of water inside the deionization chamber, and ion exchange resins are arranged in each region such that an anion exchange resin, cation exchange resin, and anion exchange resin are aligned in order from the position of the inlet of the water to be processed. In the EDI device shown in FIG. 9 as well, ion exchangers are in a multilayered-bed configuration inside deionization chamber 23.

[0050]

In the EDI device based on the present invention, an intermediate ion

exchange membrane (IEM) can be provided between the anion exchange membrane on the side facing the anode and the cation exchange membrane on the side facing the cathode in each deionization chamber, the deionization chamber being partitioned into a first small deionization chamber and a second small deionization chamber by the intermediate ion exchange membrane, and the first and second small deionization chambers can be arranged so as to communicate such that water to be processed is supplied to one small deionization chamber of the first small deionization chamber and the second small deionization chamber and the water that flows out from the one small deionization chamber flows into the other small deionization chamber. Either of an anion exchange membrane and cation exchange membrane can be used as the intermediate ion exchange membrane. If the first small deionization chamber is here assumed to be the small deionization chamber that is close to the anode and the second small deionization chamber is assumed to be the small deionization chamber that is close to the cathode, at least an anion exchanger is packed in the first small deionization chamber and at least a cation exchanger is packed in the second small deionization chamber. Catalyst particles are adsorbed to at least one of an ion exchanger inside each small deionization chamber, an intermediate ion exchange membrane, an anion exchange membrane that is provided on the side facing the anode in the first small deionization chamber, and a cation exchange membrane that is provided on the side facing the cathode in the second small deionization chamber.

[0051]

FIG. 10 shows an example of an EDI device in which the deionization chamber is partitioned by an intermediate ion exchange membrane in this way into two small deionization chambers. This EDI device has a configuration in which each deionization chamber 23 in the EDI device shown in FIG. 6 is

partitioned by intermediate ion exchange membrane 36 into first small deionization chamber 26 and second small deionization chamber 27. In this example, an anion exchange membrane is used as intermediate ion exchange membrane 36. An anion exchange resin is packed in first small deionization chamber 26 that is closer to anode 11 and a cation exchange resin is packed in second small deionization chamber 27 that is closer to cathode 12. The water that is to be processed is first supplied to second small deionization chamber 27, the outlet water from second small deionization chamber 27 is supplied to first small deionization chamber 26 such that the flow is parallel to the flow of water in second small deionization chamber 27, and deionized water is obtained as the processed water from first small deionization chamber 26. The flow of water in anode chamber 21, concentration chambers 22 and 24, and cathode chamber 25 is a countercurrent with respect to the flow of water in first and second small deionization chambers 26 and 27.

[0052]

FIG. 11 gives a schematic representation of the disassociation reaction of water realized by catalyst particles in the EDI device shown in FIG. 10. Here, catalyst particles 43 are assumed to be adsorbed to intermediate ion exchange membrane 36 that is an anion exchange membrane. When the interfaces of different types of ion exchange substances are made up from cation exchanger 41 and intermediate ion exchange membrane 36, the disassociation of water at these interfaces is promoted as shown in the figure, hydroxide ions are efficiently generated on the side of intermediate ion exchange membrane 36, and hydrogen ions are efficiently generated on the side of cation exchanger 41.

[0053]

FIG. 12 shows another example of an EDI device in which a deionization chamber is thus partitioned into two small deionization chambers by an

intermediate ion exchange membrane. This EDI device is of a configuration in which each deionization chamber 23 in the EDI device shown in FIG. 7 is partitioned by intermediate ion exchange membrane 36 into first small deionization chamber 26 that is closer to anode 11 and second small deionization chamber 27 that is closer to cathode 12. Anion exchange resin is packed in first small deionization chamber 26, and anion exchange resin and cation exchange resin is packed as a mixed bed in second small deionization chamber 27. Water to be processed is supplied to first small deionization chamber 26, the outlet water of first small deionization chamber 26 is sent to second small deionization chamber 27, and deionized water is obtained from second small deionization chamber 27. As an example, an anion exchange membrane is used for intermediate ion exchange membrane 36.

[0054]

The EDI device shown in FIG. 13 is of a configuration in which, in second small deionization chamber 27 in the EDI device shown in FIG. 12, instead of providing an anion exchange resin and a cation exchange resin in a mixed bed configuration, a cation exchange resin is arranged in the region close to the inlet of second small deionization chamber 27 and an anion exchange resin is arranged in the region close to the outlet.

EXAMPLES

[0055]

The present invention is next described in greater detail on the basis of Examples and Comparative Examples. In the Examples and Comparative Examples, the deionized water manufacturing systems or EDI devices of the above-described configurations are assembled and actually operated. In these Examples and Comparative Examples, the advantageous effects of the present invention realized by using or not using catalyst particles are verified by

selecting whether to use catalyst particles at the time of assembly.

[0056]

[Example 1 and Comparative Example 1]

The EDI devices used in Example 1 and Comparative Example 1 were of a configuration in which, in the EDI device shown in FIG. 6, the number N of repetitions of the basic construction (cell set) that is made up from anion exchange membrane (AEM) 32, deionization chamber 23, cation exchange membrane (CEM) 33, and concentration chamber 24 between anode chamber 21 and cathode chamber 25 was assumed to be "3." Cation exchange resin (CER) was packed in anode chamber 21, anion exchange resin (AER) was packed in each concentration chamber 22 and 24 and cathode chamber 25. Cation exchange resin and anion exchange resin were packed as a mixed bed (MB) in deionization chamber 23. Amberlite® IR120B (manufactured by Dow Chemical Company; reference value for apparent density: approximately 840 g/L) that is a styrene strong acid cation exchange resin having a sulfonic group as an ion exchange group was used for the cation exchange resin. Amberlite® IRA402BL (manufactured by Dow Chemical Company; reference value of apparent density: approximately 715 g/L) that is a styrene strong base anion exchange resin having a quaternary ammonium group as an ion exchange group was used for the anion exchange resin. Selemion® CME (manufactured by AGC Engineering, Co., Ltd.) was used for the cation exchange membrane, and Selemion® AME (manufactured by AGC Engineering Co., Ltd.) was used for the anion exchange membrane. The cation exchange membrane and anion exchange membrane used here are both heterogeneous ion exchange membranes. A heterogeneous ion exchange membrane is a component realized by finely pulverizing a particulate ion exchange resin and then hardening this powder by means of a thermoplastic or thermosetting binding

agent to produce a membrane form. The mechanical strength of the heterogeneous ion exchange membrane is typically superior compared to that of a homogeneous ion exchange membrane. In contrast, a homogeneous ion exchange membrane is a component in which the ion exchange resin itself is formed in membrane form.

[0057]

In Comparative Example 1, an anion exchanger in which catalyst particles were not adsorbed was used in deionization chamber 23, but in Example 1, an anion exchange resin was subjected to a process that was carried out in advance by means of catalyst particles by the following processing method, and then the anion exchange resin after the processing was mixed with a cation exchange resin and packed in deionization chamber 23. As the particles that were used in the processing of the anion exchange resin in Example 1, processing of the anion exchange resin was carried out using particles that are adsorbed to the anion exchange resin, and as a result, the particles were adsorbed to the surface of the anion exchange resin. In any case, a resin in which particles were not adsorbed was used as the ion exchange resin that is packed in anode chamber 21, concentration chambers 22 and 24, and cathode chamber 25.

[0058]

The particles that were used in Example 1 will next be described more specifically.

[0059]

In Example 1, attapulgite, which is a silicate mineral that contains the polyvalent metals magnesium and aluminum, was used as the catalyst particles. When observed under an SEM magnified at 20000 times, the range of the particle diameter of attapulgite that was used in Example 1 was from 0.02 to 10

μm. Because attapulgite is an acicular particle, the major axis was taken as the particular diameter. When measured by the same SEM image, the range of the minor axis of the attapulgite that was used was from 0.01 to 1 μm. The minor-axis diameter is the length in the direction that is orthogonal to the major-axis diameter at the position of the center of the major-axis diameter. The attapulgite (CAS number: 12174-11-7) that was used in Example 1 is a substance for which the composition formula is noted as $(\text{Mg}, \text{Al})_5\text{Si}_8\text{O}_{20} \cdot 4\text{H}_2\text{O}$, the ratio of silicon, magnesium, and aluminum converted to the mass ratio of silicon dioxide (SiO_2), magnesium oxide (MgO), and aluminum oxide (Al_2O_3) being $\text{SiO}_2 : \text{MgO} : \text{Al}_2\text{O}_3 = 65 : 13 : 12$.

[0060]

(Processing Method of Anion Exchange Resin)

The particles were dispersed in pure water and an anion exchange resin was immersed in this dispersion liquid, following which a process of causing particles to adsorb to the surface of the anion exchange resin was carried out while agitating the liquid. The amount of particles used at this time was 300 mg per one liter of anion exchange resin. The processed anion exchange resin was thoroughly washed with pure water, and, after draining the water, put into use.

[0061]

Quantification of the attapulgite was carried out by subjecting the anion exchange resin after processing to inductively coupled plasma (ICP) atomic emission spectroscopy, which revealed that the mass of attapulgite adsorbed to the anion exchange resin was 190 mg to 1 L of anion exchange resin. The specific gravity of the attapulgite is 2.4 g/cm^3 , from which the ratio of the volume of attapulgite that was adsorbed to the volume of the anion exchange resin was found to be 0.0079%. The density of the anion exchange resin can be varied by the moisture content, but if the above-described apparent density of 715 g/L is

used, the mass ratio of the attapulgite to the anion exchange resin is 0.027 mass %.

[0062]

The specifications of the EDI devices and operating conditions such as the water flow rate, the applied voltage, and the water quality of the supply water in Example 1 and Comparative Example 1 are as shown below. In the following explanation, the flow rate of water to be processed is the total amount of the flow rate of the water to be processed that is supplied to the plurality of deionization chambers 23 in the EDI device, the electrode chamber flow rate is the flow rate of supply water that is supplied to anode chamber 21 and cathode chamber 25, and the concentrated water flow rate is the sum of the flow rates of supply water that is supplied to the plurality of concentration chambers 22 and 24.

[0063]

- Deionization chamber: Dimensions 300× 100 × 10 mm; mixed bed (MB) packed (volume ratio: cation exchange resin/anion exchange resin = 1/1)
- Concentration chamber: Dimensions 300 × 100 × 5 mm; anion exchange resin (AER) packed
- Anode chamber: Dimensions: 300 × 100 × 4 mm; cation exchange resin (CER) packed
- Cathode chamber: Dimensions: 300 × 100 × 4 mm; anion exchange resin (AER) packed
- Flow rate of water to be processed: 180 L/h
- Concentrated water flow rate: 30 L/h
- Electrode water flow rate: 10 L/h
- Supply water and water to be processed: Reverse-Osmosis membrane (RO) permeated water; conductivity $5 \pm 1 \mu\text{S/cm}$
- Applied current value: 0.9 A

- Applied current density: 0.3 A/dm²

Regarding the devices of Example 1 and Comparative Example 1, operation was carried out for 1000 hours under the above-described conditions, and the operating voltage and the resistivity of the obtained deionized water were compared. The results are shown in Table 1.

[0064]

TABLE 1

	Example 1	Comparative Example 1
Particles adsorbed to anion exchange resin	attapulgate	none
Operating voltage [V]	11.9	23.2
Resistivity [MΩ•cm]	17.1	9.0

[0065]

A comparison of Example 1 and Comparative Example that does not use catalyst particles clearly shows that Example 1 is superior in terms of both the operating voltage and the water quality and thus can confirm the basic advantageous effects of the present invention.

[0066]

In Example 1, catalyst particles were adsorbed to the anion exchange resin used in the deionization chambers, but further, catalyst particles may also be adsorbed to all or a portion of the ion exchange resins used in each electrode chamber and concentration chamber that make up the EDI device.

[0067]

[Example 2-1 and 2-2 and Comparative Example 2]

The EDI devices used in Examples 2-1 and 2-2 and Comparative Example 2 were devices in which, in the EDI device shown in FIG. 10, the number N of repetitions of the basic configuration (cell set) that is made up from

anion exchange membrane 32, first small deionization chamber 26, intermediate ion exchange membrane (IEM) 36, second small deionization chamber 27, cation exchange membrane 33, and concentration chamber 24 between anode chamber 21 and cathode chamber 25 was "3." A cation exchange resin was packed in anode chamber 21 and second small deionization chamber, and an anion exchange resin was packed in each of concentration chambers 22 and 24, first small deionization chamber 26, and cathode chamber 25. An anion exchange membrane was used for intermediate ion exchange membrane 36 that partitions first small deionization chamber 26 and second small deionization chamber 27. The components used for each of the anion exchange resin, the cation exchange resin, the anion exchange membrane, and the cation exchange membrane were the same as used in Example 1. However, catalyst particles were not adsorbed to the anion exchange resin. In particular, in Examples 2-1 and 2-2, the catalyst particles referred to in the present invention were adsorbed in advance to an anion exchange membrane by the following processing method, and the anion exchange membrane to which the catalyst particles were adsorbed was used as intermediate ion exchange membrane 36. The adsorption of catalyst particles to anion exchange membranes 32 and 34 and cation exchange membranes 31 and 33 was not carried out. Attapulgit of the same standards as used in Example 1 was used as the catalyst particles. In Comparative Example 2, the adsorption of catalyst particles to anion exchange membranes was not implemented.

[0068]

(Processing Method of Anion Exchange Membrane)

An amount of 0.2 g of catalyst particles was dispersed in 1 L of pure water, and after an anion exchange membrane was immersed in this dispersion liquid, catalyst particles were adsorbed to the surface of the anion exchange

membrane while being agitated. The processed anion exchange membrane was thoroughly cleaned with pure water, and after draining the water, put into use.

[0069]

In Example 2-1 and 2-2 and Comparative Example 2, the specifications of the EDI device and operating conditions such as the water flow rate, the applied voltage, and the water quality of the supply water were as shown below.

[0070]

- First small deionization chamber: Dimensions: $300 \times 100 \times 10$ mm; anion exchange resin (AER) packed
- Second small deionization chamber: Dimensions: $300 \times 100 \times 10$ mm; cation exchange resin (CER) packed
- Applied current value: 0.9 A (Example 2-1 and Comparative Example 2); 30 A (Example 2-2)
- Applied current density: 0.3 A/dm^2 (Example 2-1 and Comparative Example 2); 10 A/dm^2 (Example 2-2)
- The concentration chamber, anode chamber, cathode chamber, flow rate of water to be processed, flow rate of concentrated water; flow rate of electrode water, the supply water and the water to be processed are each made the same as in Example 1.

[0071]

Regarding devices of Examples 2-1 and 2-2 and Comparative Example 2, operation was carried out for 1000 hours under the above-described conditions, and the operating voltage and resistivity of the obtained deionized water were compared. The results are shown in Table 2.

[0072]

TABLE 2

	Example 2-1	Example 2-2	Comparative Example 2
Particles adsorbed to anion exchange membrane	attapulgite	attapulgite	none
Applied current [A]	0.9	30	0.9
Applied current density [A/dm^2]	0.3	10	0.3
Operating voltage [V]	12.1	58.1	189.3
Resistivity [$\text{M}\Omega\cdot\text{cm}$]	16.3	17.4	15.5

[0073]

When Example 2-1 and Comparative Example 2 are compared, Example 2-1 was superior both in terms of the operating voltage and water quality, and as a result, it was confirmed that the advantageous effects of the present invention could be obtained, as with a case in which the deionization chamber is not partitioned, even for a configuration of the EDI device in which the deionization chamber is partitioned into two small deionization chambers by an intermediate ion exchange membrane. It could further be confirmed that similar advantageous effects were obtained even when catalyst particles were caused to be adsorbed not only to the ion exchanger that is packed in the deionization chamber but also to the ion exchange membrane that partitions the deionization chamber. A comparison of Example 2-2 and Comparative Example 2 clearly reveals that Example 2-2 is superior both in terms of the operating voltage and water quality regardless of being set to a high current density of $10 \text{ A}/\text{dm}^2$, and as a result, it can be seen that remarkable advantageous effects are obtained by the present invention when at least current density is in a range of from 0.3 to $10 \text{ A}/\text{dm}^2$.

[0074]

In the above-described Examples 1, 2-1, and 2-2, results were shown for

a case in which, as one example, catalyst particles are caused to adsorb to an anion exchange resin or anion exchange membrane, but the same results are obviously obtained even when catalyst particles are selected that adsorb to a cation exchange resin or cation exchange membrane. In addition, the ion exchange membranes used in the above-described Examples were all heterogeneous ion exchange membranes, but the same advantageous effects are obviously obtained even when homogeneous ion exchange membrane are used. Further, ion exchange membranes were used that had undergone a process in which catalyst particles were caused to adsorb in the above-described Examples, but the same advantageous effects are obviously obtained as shown in the above-described Examples even when using ion exchange membranes that have been formed using ion exchange resin to which catalyst particles have been adsorbed in advance. Cases of using ion exchange membranes that have been formed using ion exchange resin to which catalyst particles have been adsorbed in advance also come within the category of the present invention.

[0075]

Similarly, in the above-described Example 2-1 and 2-2, catalyst particles were adsorbed to, of the anion exchange membranes used in an EDI device, the entire surfaces of the intermediate ion exchange membrane that further partitions the deionization chamber into small deionization chambers, but catalyst particles may also be adsorbed to another ion exchange membrane of the EDI device, or further, catalyst particles may also be adsorbed to one surface of an ion exchange membrane or to only specific sites of an ion exchange membrane. In Examples 2-1 and 2-2 in particular, an anion exchange membrane was selected as the intermediate ion exchange membrane that partitions a deionization chamber into small deionization chambers, but the

advantageous effects of the present invention are obviously obtained when a cation exchange membrane is used as the intermediate ion exchange membrane. In this case, adsorbing catalyst particles to a cation exchange membrane or adsorbing catalyst particles to an anion exchange resin that is packed in any of the small deionization chambers can be selected as appropriate.

[0076]

[Example 3 and Comparative Example 3]

In Example 3 and Comparative Example 3, the EDI devices were of the same configurations as in Example 1 and Comparative Example 1, and the dimensions of the deionization chambers, concentration chambers, anode chambers, and cathode chambers as well as the packed ion exchange resins were the same as in Example 1, but EDI devices were used in which the number N of repetitions of cell sets was "1." In the device of Example 3, the catalyst particles that were used are of the same standards as used in Example 1, and the method of processing the anion exchange resin was the same as in Example 1.

[0077]

Pure water in which the conductivity was no greater than 1 $\mu\text{S}/\text{cm}$ was used as the water to be processed and the supply water, the flow rate of the water to be processed was set to 60 L/h, the flow rate of the concentrated water was set to 10 L/h, and the flow rate of the electrode water was set to 10 L/h. Voltage was then applied to the EDI device to achieve the applied current density that is shown in the column for the applied current density of Table 3, and the operating voltage was found after the passage of one hour. The results are shown in Table 3. In Table 3, the arrows indicate the behavior of the voltage at the time of measurement, a rightward arrow ($\rightarrow$) indicating a stable trend and

an upward arrow (↑) indicating a rising trend. The indication of the behavior of the voltage by means of arrows is similar in each of the following tables.

[0078]

TABLE 3

	Example 3		Comparative Example 3	
Particles adsorbed to anion exchange resin	attapulgate		none	
Applied current density [A/dm ²]	0.3	10	0.3	10
Operating voltage [V]	4.0 →	17 →	4.7 ↑	30 ↑

[0079]

The results of Example 3 and Comparative Example 3 clearly show that the operating voltage exhibits a rising trend when the conductivity of the water to be processed is low and that the operating voltage rises markedly when processing by means of catalyst particles is not carried out, thereby preventing operation at a practical applied current density.

[0080]

[Example 4 and Comparative Example 4]

The EDI devices were the same as in Example 3 and Comparative Example 3, but only Amberlite® IRA402BL (manufactured by Dow Chemical Company; reference value of apparent density: approximately 715 g/L) that is a styrene highly basic anion exchange resin having a quaternary ammonium group as an ion exchange group was used as the ion exchanger that is packed in the deionization chamber, and the deionization chamber was made a single-bed configuration. Regarding the anion exchange resin used in Example 4, the same process as was described in Example 1 was carried out in advance to adsorb attapulgate to the surface. The water to be processed and supply water were the same as used in Example 3, the water flow rates to each chamber

were the same as used in Example 3, voltage was applied to the EDI device to realize the applied current density shown in the column of applied current density of Table 4, and the operating voltage was found after the passage of one hour.

[0081]

TABLE 4

	Example 4		Comparative Example 4	
Particles adsorbed to anion exchange resin	attapulgate		none	
Applied current density [A/dm^2]	0.3	0.8	0.3	0.8
Operating voltage [V]	4.3 →	5.3 →	61 ↑	97 ↑

[0082]

The results of Example 4 and Comparative Example 4 reveal that, compared to a case in which a mixed-bed ion exchange resin is packed in the deionization chamber as in Examples 1 and 3, the effect of causing the adsorption of catalyst particles was particularly increased when a single-bed ion exchange resin was packed.

[0083]

[Example 5]

The deionized water manufacturing system shown in FIG. 1 was assembled. The EDI device used in Example 2-1 in which the number N of repetitions of cell sets is "5" was used as the EDI device that is provided in the deionized water manufacturing system. The ion exchange resin and ion exchange membrane as well as the dimensions of each chamber were the same as used in Example 2-1, but the adsorption of catalyst particles to the ion exchange membrane was not carried out. Instead of adsorption to the ion exchange membrane, attapulgate was adsorbed in advance to the anion

exchange resin used in the EDI device by the same method as was shown in Example 1, and the intermediate ion exchange membrane that was an anion exchange membrane in Example 2-1 was changed to a cation exchange membrane. The adoption of this configuration enables the promotion of the water disassociation reaction between the intermediate ion exchange membrane and the anion exchange resin in which the attapulgite has been adsorbed of the first small deionization chamber. In Example 5, permeated water that had passed through two passes of reverse-osmosis membrane devices was used as the water to be processed of the EDI device, the conductivity of this water being $2 \pm 1 \mu\text{S}/\text{cm}$, the sodium concentration being $100 \mu\text{g}/\text{L}$, and the silica concentration being $50 \mu\text{g}/\text{L}$. Reverse-osmosis membrane permeated water was used as the supply water.

[0084]

With the flow rate of the water to be processed set to 800 L/h, the flow rate of concentrated water set to 80 L/h, the flow rate of electrode water set to 20 L/h, and the applied current density at $0.5 \text{ A}/\text{dm}^2$, the water quality of deionized water flowing from the EDI device and the operating voltage were found. The results are shown in Table 5.

[0085]

TABLE 5

	Example 5
Water quality of deionized water [$\text{M}\Omega\cdot\text{cm}$]	17.9
Applied current density [A/dm^2]	0.5
Operating voltage [V]	19 →

[0086]

The results of Example 5 reveal that the current density in an EDI device can be made large, and moreover, the flow rate of the water to be processed

can be made high even when using water to be processed that has a low residual ion concentration and low conductivity such as permeated water passing through two passes of reverse-osmosis membrane devices. When the flow rates of the water to be processed per cell set in the EDI devices are compared, the flow rate in Example 5 is 2.67 times that of Example 2.

[0087]

[Example 6]

The deionized water manufacturing system shown in FIG. 3 was assembled. Two EDI devices 10 and 15 connected in a series were used in this deionized water manufacturing system, but both EDI devices 10 and 15 that were used were identical to the EDI device described in Example 5. By not only providing reverse-osmosis membrane devices 51 and 52 connected in two passes but also using EDI devices 10 and 15 in two passes, the water to be processed that is supplied to second-pass EDI device 10 had an extremely low conductivity of $16 \pm 2 \text{ M}\Omega \cdot \text{cm}$ (*i.e.*, a conductivity of $0.0635 \pm 0.008 \text{ }\mu\text{S/cm}$), and in addition, had a boron concentration of $1 \pm 0.2 \text{ }\mu\text{g/L}$. Reverse-osmosis membrane-permeated water was used as the supply water of first-pass EDI device 15 and the processed water of first-pass EDI device 15, *i.e.*, deionized water from first-pass EDI device 15, was used as the supply water of second-pass EDI device 10.

[0088]

In first-pass EDI device 15, the flow rate of water to be processed was set to 570 L/h, the concentrated water flow rate was set to 50 L/h, the electrode water flow rate was set to 20 L/h; and in second-pass EDI device 10, the flow rate of water to be processed was set to 500 L/h, the flow rate of concentrated water was set to 50 L/h, and the electrode water flow rate was set to 20 L/h. The applied current density was set to 0.8 A/dm^2 for each of EDI devices 10 and

15, and the water quality and boron concentration of deionized water flowing from second-pass EDI device 10 and operating voltage were then found. The results are shown in Table 6.

[0089]

TABLE 6

	Example 6
Water quality of deionized water [$\text{M}\Omega\cdot\text{cm}$]	18.2
Boron concentration of deionized water [ng/L]	Less than 10
Applied current density [A/dm^2]	0.8
Operating voltage [V]	14 $\rightarrow$

[0090]

When EDI devices are connected in two passes and deionized water having an extremely low impurity concentration is to be obtained, the conductivity of the water to be processed that is supplied to the second-pass EDI device is low, whereby the increase of the operating voltage of the second-pass EDI device becomes a concern, but the results of Example 6 reveal that the use of EDI devices that are based on the present invention can suppress increase of the operating voltage. Deionized water of higher purity can be easily obtained on the basis of the present invention. In addition, although boron is known to be an element that is difficult to remove by an ordinary deionization process, it was found that boron could be removed to the order of ng/L by means of Example 6.

[0091]

[Example 7]

The deionized water manufacturing system shown in FIG. 1 was assembled. The EDI device shown in FIG. 8 was used as the EDI device provided in the deionized water manufacturing system, and the number N of

repetitions of cell sets was “5.” The deionization chamber was of a multilayer-bed configuration such that a cation exchange resin layer, an anion exchange resin layer, a cation exchange resin layer, and an anion exchange resin layer were arranged in that order from the upstream side along the flow of the water to be processed. The ion exchange membrane and ion exchange resin that were used are the same as the case of Example 1, and attapulgite was adsorbed to the anion exchange resin in advance by a processing method that is the same as Example 1. The dimensions of the deionization chambers, concentration chambers, anode chamber, and cathode chamber were the same as the case of Example 1. In Example 7, permeated water that had passed through two passes of reverse-osmosis membrane devices was used as the water to be processed of the EDI device, and the conductivity of this water to be processed was $1.5 \pm 0.2 \mu\text{S/cm}$. Reverse-osmosis membrane-permeated water was used as the supply water.

[0092]

The flow rate of the water to be processed was set to 1000 L/h, the concentrated water flow rate was set to 100 L/h, the electrode water flow rate was set to 20 L/h, the applied current density was set to 0.6 A/dm^2 , and the operating voltage that was measured after operating for 1000 hours was 18 V.

[0093]

Comparison of Example 1 and Example 7 reveals that the operating voltage per cell set was 4.0 V in Example 1 but 3.6 V in Example 7. The current density in Example 7 was twice that of Example 1, and even though the conductivity of the water to be processed was lower in Example 7, the fact that the operating voltage per cell set was lower in Example 7 than in Example 1 shows that making the configuration of the ion exchanger in the deionization chamber a multilayer-bed configuration rather than a mixed-bed configuration

obtains a more marked advantageous effect that results from causing the adsorption of attapulgite to the anion exchange resin. In addition, a comparison of the flow rate of water to be processed per cell set of the EDI device shows that the flow rate in Example 7 was 3.33 times that of the flow rate in Example 1.

REFERENCE SIGN LIST

[0094]

10, 15	Electrodeionization device (EDI device);
11	Anode;
12	Cathode;
51, 52	Reverse-osmosis membrane device;
21	Anode chamber;
22, 24	Concentration chamber;
26	First small deionization chamber;
27	Second small deionization chamber;
23	Deionization chamber;
25	Cathode chamber;
31, 33	Cation exchange membrane (CEM);
32, 34	Anion exchange membrane (AEM);
36	Intermediate ion exchange membrane (IIEM);
41	Cation exchanger;
42	Anion exchanger;
43	Catalyst particles.

CLAIMS

1. A deionized water manufacturing system that is supplied with raw water and that manufactures deionized water, comprising:
 - a reverse-osmosis membrane device to which raw water is supplied; and
 - an electrodeionization device that includes a deionization chamber which is partitioned by an ion exchange membrane and to which permeated water of the reverse-osmosis membrane device is supplied,
 - wherein an ion exchanger is packed inside the deionization chamber, and
 - wherein particles containing polyvalent metal are adsorbed to at least one surface of at least one portion of the ion exchange membrane and at least one portion of the ion exchanger.
2. The deionized water manufacturing system as set forth in claim 1, wherein the ion exchanger packed in the deionization chamber is either one of an anion exchanger and a cation exchanger.
3. The deionized water manufacturing system as set forth in claim 1, wherein, in the deionization chamber, a cation exchanger and an anion exchanger are alternately arranged along a direction of flow of water in the deionization chamber.
4. The deionized water manufacturing system as set forth in any one of claims 1 to 3, wherein the reverse-osmosis membrane device comprises a configuration in which devices each equipped with a reverse-osmosis membrane are connected in a two-pass series.

5. The deionized water manufacturing system as set forth in any one of claims 1 to 4, wherein, in the permeated water that is supplied to the deionization chamber of the electrodeionization device, sodium concentration is 100 µg/L or less, and silica concentration is 50 µg/L or less.

6. The deionized water manufacturing system as set forth in any one of claims 1 to 5, wherein a conductivity of the permeated water that is supplied to the deionization chamber of the electrodeionization device is 3 µS/cm or less.

7. The deionized water manufacturing system as set forth in any one of claims 1 to 6, further comprising an additional electrodeionization device between the reverse-osmosis membrane device and the electrodeionization device,

wherein the permeated water of the reverse-osmosis membrane device is supplied to the deionization chamber of the electrodeionization device by way of a deionization chamber of the additional electrodeionization device.

8. The deionized water manufacturing system as set forth in claim 7, wherein the electrodeionization device is operated such that the boron concentration in deionized water that is discharged from the deionization chamber of the electrodeionization device is 10 ng/L or less.

9. The deionized water manufacturing system as set forth in any one of claims 1 to 8, wherein the particles are composed of silicate.

10. The deionized water manufacturing system as set forth in claim 9, wherein the particles are composed of at least one of aluminum silicate,

magnesium silicate, calcium silicate, calcium-magnesium silicate, aluminosilicate, and a silicate mineral.

11. The deionized water manufacturing system as set forth in claim 10, wherein the particles are composed of at least one of attapulgite, sepiolite, and wollastonite.

12. An electrodeionization device that is equipped with at least one deionization chamber between an anode chamber that is provided with an anode and a cathode chamber that is provided with a cathode, the deionization chamber being partitioned by an anion exchange membrane that is positioned on a side facing the anode and a cation exchange membrane that is positioned on a side facing the cathode, and at least one of an anion exchanger and a cation exchanger being packed inside the deionization chamber, characterized in that:

particles containing polyvalent metal are caused to adsorb to at least one surface of the anion exchange membrane, the cation exchange membrane, the anion exchanger, and the cation exchanger.

13. The electrodeionization device as set forth in claim 12, wherein the particles are composed of silicate.

14. The electrodeionization device as set forth in claim 13, wherein the particles are composed of at least one of aluminum silicate, magnesium silicate, calcium silicate, calcium-magnesium silicate, aluminosilicate, and a silicate mineral.

15. The electrodeionization device as set forth in claim 14, wherein the particles are composed of at least one of attapulgite, sepiolite, and wollastonite.

16. The electrodeionization device as set forth in any one of claims 12 to 15, wherein the particles are absorbed on the surface of at least one of the anion exchange membrane and the anion exchanger.

17. The electrodeionization device as set forth in any one of claims 12 to 16, wherein at least one of the anion exchange membrane and the cation exchange membrane is a heterogeneous ion exchange membrane.

18. The electrodeionization device as set forth in any one of claims 12 to 17, wherein volume of the particles with respect to volume of the anion exchanger and the cation exchanger is less than 1 volume %.

19. The electrodeionization device as set forth in any one of claims 12 to 18, wherein either one of the anion exchanger and the cation exchanger is packed in said deionization chamber.

20. The electrodeionization device as set forth in any one of claims 12 and 18, wherein the anion exchanger and the cation exchanger are alternately arranged in the deionization chamber along a direction of flow of water in the deionization chamber.

21. The electrodeionization device as set forth in any one of claims 12 to 18, wherein:

the deionization chamber is provided with an intermediate ion exchange

membrane that is positioned between the anion exchange membrane and the cation exchange membrane and is partitioned into a first small deionization chamber and second small deionization chamber by the intermediate ion exchange membrane;

at least the anion exchanger is packed in the first small deionization chamber that is partitioned by the anion exchange membrane and the intermediate ion exchange membrane;

at least the cation exchanger is packed in the second small deionization chamber that is partitioned by the cation exchange membrane and the intermediate ion exchange membrane; and

the first small deionization chamber and the second small deionization chamber communicate such that the water to be processed is supplied to one small deionization chamber of the first small deionization chamber and the second small deionization chamber and water that flows out from the one small deionization chamber flows into the other small deionization chamber.

22. The electrodeionization device as set forth in claim 21, wherein the particles are adsorbed to a surface of the intermediate ion exchange membrane.

23. A deionized water manufacturing method that uses the electrodeionization device as set forth in any one of claims 12 to 22, wherein deionized water is obtained by causing water to be processed to flow through the deionization chamber while applying a dc voltage between the anode and the cathode such that current density in the deionization chamber is at least 0.3 A/dm² but no greater than 10 A/dm².

24. A deionized water manufacturing method that uses an

electrodeionization device which is equipped with at least one deionization chamber between an anode chamber provided with an anode and a cathode chamber provided with a cathode and in which the deionization chamber is partitioned by an anion exchange membrane that is positioned on a side facing the anode and a cation exchange membrane that is positioned on a side facing the cathode, at least one of an anion exchanger and a cation exchanger being packed inside the deionization chamber, characterized by comprising steps of:

causing particles that contain polyvalent metal to be adsorbed to a surface of at least one of the anion exchange membrane, the cation exchange membrane, the anion exchanger, and the cation exchanger; and

after the step of causing the adsorption, obtaining deionized water by causing water that is to be processed to flow through the deionization chamber while applying a dc voltage between the anode and the cathode.

25. An ion exchange membrane for electrodeionization device, the ion exchange membrane being used in an electrodeionization device which is equipped with at least one deionization chamber between an anode chamber provided with an anode and a cathode chamber provided with a cathode, at least one of an anion exchanger and a cation exchanger being packed inside the deionization chamber, the ion exchange membrane being at least one of an anion exchange membrane that partitions the deionization chamber and that is positioned on a side facing the anode in the deionization chamber, a cation exchange membrane that partitions the deionization chamber and that is positioned on a side facing the cathode in the deionization chamber, and an intermediate ion exchange membrane that further partitions the inside of the deionization chamber into small deionization chambers, the ion exchange membrane characterized in that

particles that contain polyvalent metal are caused to be adsorbed to a surface of the ion exchange membrane.

26. An ion exchanger for electrodeionization device, the ion exchanger being used in an electrodeionization device which is equipped with at least one deionization chamber between an anode chamber provided with an anode and a cathode chamber provided with a cathode, the deionization chamber being partitioned by an anion exchange membrane that is positioned on a side facing the anode and a cation exchange membrane that is positioned on a side facing the cathode, the ion exchanger including at least one of anion exchanger and cation exchanger and being packed inside the deionization chamber, the ion exchanger characterized in that:

particles that contain polyvalent metal are caused to be adsorbed to a surface of the ion exchanger.