

METHOD FOR OPERATING ELECTRODEIONIZATION DEIONIZED WATER PRODUCING
APPARATUS, ELECTRODEIONIZATION DEIONIZED WATER PRODUCING SYSTEM,
AND ELECTRODEIONIZATION DEIONIZED WATER PRODUCING APPARATUS

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BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an electrodeionization
(hereinafter simply referred to as "EDI") deionized water producing
10 apparatus used in the fields of various industries such as
semiconductor manufacture, pharmaceutical manufacture, power
generation such as fossil-fueled and nuclear power generation, and
food industry and in research facilities.

2. Description of the Related Art

15 As a method for producing deionized water, conventionally,
a method is known in which water to be treated is forced through
ion exchange resins. In this method, however, when the ion exchange
resins are exhausted with impurity ions, it is necessary to apply
a regeneration process using chemical reagents. In order to overcome
20 disadvantages associated with such a treatment operation, a
deionization deionized water producing method has been developed
and commercialized using EDI which does not require regeneration
using chemical reagents.

In the conventional EDI, cation exchange membranes and anion
25 exchange membranes are alternately placed spaced from each other

and an ion exchanger is filled in every other space formed between the cation and anion exchange membranes to form desalination chambers. Power saving EDIs in which the structure of the desalination chamber is fundamentally changed have been developed in place of the conventional EDI.

Such a power saving EDI is described in, for example, Japanese Patent Laid-Open Publication No. 2001-239270 and has a structure in which ion exchanger(s) is filled in two small desalination chambers formed by a cation exchange membrane on one side, an anion exchange membrane on the other side, and an intermediate ion exchange membrane positioned between the cation exchange membrane and the anion exchange membrane to form a desalination chamber consisting of the two small desalination chambers, a concentrating chamber is provided on both sides of the desalination chamber via the cation exchange membrane and the anion exchange membrane, and the desalination chamber and the concentrating chambers are placed between an anode chamber having an anode and a cathode chamber having a cathode. While a voltage is applied, water to be treated is passed through one of the small desalination chambers, the water flowing out of the small desalination chamber is passed through the other small desalination chamber, and concentrate water is passed through the concentrating chambers to remove impurity ions derived from the water to be treated, to obtain deionized water. With an EDI of this structure, it is possible to employ a configuration, for example, having a single ion exchanger of only an anion exchanger or only

a cation exchanger or having a mixed exchanger of an anion exchanger and a cation exchanger as the ion exchanger to be filled into at least one of the two small desalination chambers. With such a configuration, it is possible to reduce the electrical resistance based on the type of the individual ion exchanger and to set the thickness to an optimum thickness of the ion exchanger for achieving a high performance.

When, however, the hardness of the water to be treated flowing into the EDI is high, scales consisting of calcium carbonate, magnesium hydroxide, or the like may be formed in the concentrating chamber of the EDI. When scales are formed, the electrical resistance at the portion in which the scales are formed increases and it becomes more difficult for the current to flow. In other words, in order to apply a current having the same current value as in the case in which no scale is formed, the voltage must be increased, and thus, the power consumption increases. In addition, depending on the place of adhesion of scales, the current density may vary within the concentrating chamber, resulting in unevenness of current within the desalination chamber. Moreover, when the amount of adhesion of scales is further increased, the differential pressure through the system is increased and the voltage is further increased, and, when the voltage exceeds the maximum voltage of the apparatus, the current value is reduced. In this case, a current necessary for removing ions cannot be applied, resulting in degradation of quality of treated water. Furthermore, there is also a possibility that

grown scales intrude into the ion exchange membrane to ultimately break the ion exchange membrane.

As a countermeasure for solving this problem, a method is known in which water to be treated having a low hardness is passed through the EDI. If the hardness of the water to be treated is low, the solubility product is not reached inside the concentrating chamber, product and therefore, no scale will be formed. However, in reality, even when such water to be treated having a low hardness is passed through and treated, there are cases in which scales of calcium carbonate, magnesium hydroxide, etc. are formed within the concentrating chamber. In these cases, problems similar to those described above would be encountered.

Japanese Patent Laid-Open Publication No. 2001-225078 discloses an EDI in which an anion exchanger having a specific structure is placed on the side of the concentrating chamber near an anion exchange membrane. With this EDI, a diffusive dilution of OH^- ions to the concentrating liquid is accelerated by a surface of a porous anion exchanger and the OH^- ion concentration on the surface is quickly reduced. On the other hand, it becomes more difficult for hardness ions to intrude into the inside of the porous anion exchanger, resulting in reduced number of opportunities of contact between the OH^- ions and the hardness ions, and, consequently, inhibition of deposition and accumulation of hardness components.

Japanese Patent Laid-Open Publication No. 2002-1345 discloses an EDI in which an ion exchanger to be stored in a concentrating

chamber includes at least two layers having different water permeability with the layer having a smaller water permeability being provided on the side of the anion exchange membrane and having anion exchange groups at least on its surface. With this EDI, when concentrated liquid which has moved through the layer with a larger water permeability and having a large amount of hardness components reaches the layer with the smaller water permeability, the mobility of hardness components is reduced. Hence, flow of hardness components into the surface of the side of the anion exchange membrane near the concentrating chamber is prevented, and deposition and accumulation of hardness components are inhibited.

In Japanese Patent Laid-Open Publication Nos. 2001-225078 and 2002-1345, however, the conditions for the water to be supplied to the concentrating chamber are not specified and it is not clear whether or not the scale formation can be prevented in a long-term operation. In addition, there is no description of any influences of the invention on the quality of EDI-treated water.

As the water to be supplied to the EDI, typically, permeated water of a reverse osmosis membrane in which tap water or industrial water is roughly desalinated is used. In a reverse osmosis membrane, ion components are removed, but most of gases permeates through and is not removed. As such, free carbon dioxide of high concentration which permeates through the membrane as carbon dioxide gas will remain within the permeated water of the reverse osmosis membrane. The free carbon dioxide is an anionic load on the EDI,

and, because the free carbon dioxide is a weak acid, it tends to remain in the treated water, bringing about inferior water quality. Because of this, a carbon dioxide removal device such as a membrane degassing apparatus is provided upstream of the EDI to thereby supply
5 water in which carbonic acid is removed to the EDI to reduce the load of carbonic acid and to consequently improve the quality of the treated water. Moreover, this method for providing a carbon dioxide removal device is also effective for improving the silica removal performance which is more difficult to remove than carbon
10 dioxide. Therefore, when a high purity is required for the quality of the treated water, a carbon dioxide removal device is required.

However, even when a carbon dioxide removal device is provided upstream of the EDI, the treated water of the carbon dioxide removal device is used as the water to be treated in the EDI and the concentrate
15 water in the EDI, and an anion exchanger is provided in the concentrating chamber on the side of the anion exchange membrane near the anode in order to obtain high purity quality of the treated water, there are cases in which scales of hardness components or the like are formed in a long-term operation.

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SUMMARY OF THE INVENTION

The present invention advantageously provides an EDI in which water having free carbon dioxide is supplied to a concentrating chamber filled with an anion exchanger on the side of an anion exchange
25 membrane near an anode. With this structure, formation of scales

within the concentrating chamber can be inhibited even in a long-term operation. In addition, an anion exchanger is placed within the concentrating chamber on the side of an anion exchange membrane near an anode and a water permeating material having no strong basic anion exchange group is provided between said anion exchanger and a cation exchange membrane. With such a structure, because the anion exchanger substantially does not come in contact with the cation exchange membrane, bicarbonate ions which have passed through the anion exchanger are diffused to the downstream along with the concentrate water before the bicarbonate ions reach the cation exchange membrane, and thus, degradation in the quality of treated water can be prevented.

According to a first aspect of the present invention, there is provided an EDI deionized water producing apparatus comprising, between an anode chamber having an anode and a cathode chamber having a cathode, a desalination chamber in which a side near the anode is separated by an anion exchange membrane and a side near the cathode is separated by a cation exchange membrane, and a concentrating chamber in which a side near the anode is separated by a cation exchange membrane, a side near the cathode is separated by an anion exchange membrane, and an anion exchanger is filled in the anode side of the anion exchange membrane. In the EDI deionized water producing apparatus, water having free carbon dioxide is supplied to the concentrating chamber.

A mechanism for the formation of scales within the EDI will

now be described. When a current is applied in an EDI, carbonic acid (carbon dioxide) (a collective term which includes free carbon dioxide, bicarbonate ions, and carbonate ions) in the water to be treated is captured by an anion exchange resin as carbonate ions
5 by actions of a large amount of hydroxide ions generated by dissociation of water in the desalination chamber. The carbonate ions pass through the anion exchange membrane on the side near the anode along with hydroxide ions and other anions such as chloride ions captured by the resin and move to the concentrating chamber.
10 Because of this, the pH in a region of the concentrating chamber near the anion exchange membrane locally becomes alkaline. Likewise, hardness ions such as calcium ions and magnesium ions captured by a cation exchange resin and passed through the cation exchange membrane accumulate on the surface of the anion exchange membrane
15 in the concentrating chamber. Then, the carbonate ions and the hydroxide ions come in contact with the calcium ions and magnesium ions, resulting in deposition of calcium carbonate and magnesium hydroxide as scales.

When an anion exchanger is present on the anode side of the
20 anion exchange membrane in the concentrating chamber as in the first aspect of the present invention, the carbonate ions and hydroxide ions passing through the anion exchange membrane do not move to the concentrate water, but instead, pass through the anion exchanger having a high conductivity. In this process, when free carbon dioxide
25 is included in the concentrating water flowing through the

concentrating chamber, the free carbon dioxide reacts with the carbonate ions and hydroxide ions flowing through the anion exchanger to form bicarbonate ions. The bicarbonate ions are finally discharged into the concentrate water on the anode side of the anion
5 exchanger. Because calcium bicarbonate and magnesium bicarbonate are far less likely to be deposited than calcium carbonate and magnesium hydroxide, generation of scales within the concentrating chamber can be inhibited. In addition, the bicarbonate ions released into the concentrate water reacts with hydrogen ions which have passed
10 through the cation exchange membrane from the other side to form free carbon dioxide. The free carbon dioxide thus obtained can then react with the carbonate ions and hydroxide ions within the ion exchanger downstream of the concentrating chamber. In this manner, according to this aspect of the present invention, a shift in pH
15 which may otherwise occur within the concentrating chamber near the anion exchange membrane can be alleviated.

According to a second aspect of the present invention, there is provided an EDI deionized water producing apparatus comprising, between an anode chamber having an anode and a cathode chamber having
20 a cathode, a desalination chamber in which a side near the anode is demarcated by an anion exchange membrane and a side near the cathode is demarcated by a cation exchange membrane, and a concentrating chamber in which a side near the anode is demarcated by a cation exchange membrane and a side near the cathode is demarcated
25 by an anion exchange membrane and which concentrating chamber is

filled with a mixture ion exchanger of an anion exchanger and a cation exchanger. Water having free carbon dioxide is supplied to the concentrating chamber. In the second aspect of the present invention, because a cation exchanger for supplying hydrogen is
5 mixed with an anion exchanger and the mixture exchanger is used to fill the chamber, the bicarbonate ions moving through the anion exchanger become free carbon dioxide before the bicarbonate ions reach the cation exchanger by an action of hydrogen ions supplied from the cation exchanger and are released into the concentrate
10 water. Because of this, it is possible to prevent an increase in a concentration of free carbon dioxide near the cation exchange membrane and to alleviate influences upon the quality of the treated water.

According to a third aspect of the present invention, it is
15 preferable that, in the structure of the first aspect of the present invention, in the concentrating chamber, an anion exchanger is provided on the anode side of the anion exchange membrane and a water permeating material which does not have a strong basic anion exchange group is provided between the anion exchanger and the cation
20 exchange membrane.

According to the third aspect of the present invention, because the anion exchanger does not come in contact the cation exchange membrane in the concentrating chamber, the concentration of the free carbon dioxide near the cation exchange membrane does not
25 increase, and thus, it is possible to prevent degradation of quality

of the treated water. Specifically, because a water permeating material having no strong basic anion exchange group is provided on the side near the cation exchange membrane, the bicarbonate ions moving from the anion exchanger cannot further move to the side near the cation exchange membrane at the water permeating material, and are released from the anion exchanger and become free carbon dioxide. This free carbon dioxide is diffused to the downstream along with the concentrate water flowing through the water permeating material, and thus, it is possible to prevent the concentration of free carbon dioxide from increasing near the cation exchange membrane.

According to a fourth aspect of the present invention, it is preferable that, in the structure of the second aspect of the present invention, the mixture ion exchanger filled into the concentrating chamber is a mixture ion exchanger in which the percentage of cation exchanger is increased from the side near the anion exchange membrane toward the cation exchange membrane. According to the fourth aspect of the present invention, in addition to the advantages identical to those in structure of the second aspect, because the percentage of the anion exchanger at the side near the cation exchange membrane is low, the concentration of the free carbon dioxide near the cation exchange membrane can be more reliably reduced.

According to a fifth aspect of the present invention, it is preferable that the water to be supplied to the concentrating chamber has a concentration of free carbon dioxide of $0.5 \text{ mg-CO}_2/\text{l} - 200$

mg-CO₂/l. Therefore, it is possible to use, for example, water pretreated with a reverse osmosis membrane in which tap water or industrial water is roughly desalinated.

According to a sixth aspect of the present invention, there is provided an EDI deionized water producing apparatus (EDI) comprising, between an anode chamber having an anode and a cathode chamber having a cathode, a desalination chamber in which a side near the anode is demarcated by an anion exchange membrane and a side near the cathode is demarcated by a cation exchange membrane, and a concentrating chamber having a side near the anode demarcated by a cation exchange membrane, a side near the cathode demarcated by an anion exchange membrane, and the anode side of the anion exchange membrane is filled with an anion exchanger. Pipes are provided and connected such that treated water of a decarbonator device provided upstream of the EDI deionized water producing apparatus is introduced into a feed pipe of the water to be treated by the EDI deionized water producing apparatus and the water to be treated by the decarbonator device is introduced into a feed pipe of concentrate water of the EDI deionized water producing apparatus.

According to a seventh aspect of the present invention, there is provided an EDI deionized water producing apparatus comprising, between an anode chamber having an anode and a cathode chamber having a cathode, a desalination chamber in which a side near the anode is demarcated by an anion exchange membrane and a side near the cathode is demarcated by a cation exchange membrane, and a

concentrating chamber in which a side near the anode is demarcated by a cation exchange membrane and a side near the cathode is demarcated by an anion exchange membrane, and which concentrating chamber is filed with a mixture ion exchanger of an anion exchanger and a cation
5 exchanger. Pipes are provided and connected such that treated water of a decarbonator device provided upstream of the EDI deionized water producing apparatus is introduced into a feed pipe for water to be treated by the EDI deionized water producing apparatus and the water to be treated by the decarbonator device is introduced
10 into a feed pipe of concentrate water of the EDI deionized water producing apparatus.

According to an eighth aspect of the present invention, it is preferable that, in the EDI deionized water producing apparatus according to the seventh aspect of the present invention, the mixture
15 ion exchanger in the concentrating chamber is a mixture ion exchanger in which a percentage of the cation exchanger increases from the side near the anion exchange membrane toward the cation exchange membrane.

According to a ninth aspect of the present invention, there
20 is provided an EDI deionized water producing apparatus comprising, between an anode chamber having an anode and a cathode chamber having a cathode, a desalination chamber in which a side near the anode is demarcated by an anion exchange membrane and a side near the cathode is demarcated by a cation exchange membrane, and a
25 concentrating chamber in which a side near the anode is demarcated

by a cation exchange membrane, a side near the cathode is demarcated by an anion exchange membrane, an anion exchanger is provided at the anode side of the anion exchange membrane, and a water permeating material having no strong basic anion exchange group is provided
5 between the anion exchanger and the cation exchange membrane.

According to a tenth aspect of the present invention, there is provided an EDI deionized water producing apparatus in which the upstream decarbonator device is omitted and permeate water of a reverse osmosis membrane device is directly used as the water
10 to be treated and water to be supplied to the concentrating chamber, the EDI deionized water producing apparatus comprising, between an anode chamber having an anode and a cathode chamber having a cathode, a desalination chamber in which a side near the anode is demarcated by an anion exchange membrane and a side near the cathode
15 is separated by a cation exchange membrane and which has two small desalination chambers separated by an intermediate ion exchange membrane provided between the anion exchange membrane and the cation exchange membrane, and a concentrating chamber in which a side near the anode is separated by a cation exchange membrane and a side
20 near the cathode is separated by an anion exchange membrane and which is filled with a mixture ion exchanger of an anion exchanger and a cation exchanger.

According to an eleventh aspect of the present invention, there is provided an EDI deionized water producing apparatus in which
25 the upstream decarbonator device is omitted and permeate water of

a reverse osmosis membrane device is directly used as water to be treated and water to be supplied to a concentrating chamber, the EDI deionized water producing apparatus comprising, between an anode chamber having an anode and a cathode chamber having a cathode, a desalination chamber in which a side near the anode is separated by an anion exchange membrane and a side near the cathode is separated by a cation exchange membrane and which has two small desalination chambers separated by an intermediate ion exchange membrane provided between the anion exchange membrane and the cation exchange membrane, and a concentrating chamber in which a side near the anode is separated by a cation exchange membrane, a side near the cathode is separated by an anion exchange membrane, an anion exchanger is placed on the anode side of the anion exchange membrane, and water permeating material having no strong basic anion exchange group is provided between the anion exchanger and the cation exchange membrane.

With these EDI deionized water producing apparatus, it is possible to reliably apply a method for operating an EDI deionized water producing apparatus as described above. In particular, in an EDI deionized water producing apparatus having a desalination chamber with two small desalination chambers separated by an intermediate ion exchange membrane provided between the anion exchange membrane and the cation exchange membrane, it is possible to omit the pretreatment decarbonator device and to use the permeate water of the reverse osmosis membrane device directly as the water to be treated and water to be supplied to the concentrating chamber,

resulting in a reduction of installation cost.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram showing an EDI deionized water
5 producing system according to a preferred embodiment of the present invention.

Fig. 2 is a schematic diagram showing an EDI deionized water producing system according to another preferred embodiment of the present invention.

10 Fig. 3 is a schematic diagram showing an EDI deionized water producing system according to still another preferred embodiment of the present invention.

Fig. 4 is a schematic diagram showing an EDI deionized water producing system according to yet another preferred embodiment of.
15 the present invention.

Fig. 5 is a simplified diagram showing a structure of an EDI deionized water producing apparatus according to a preferred embodiment of the present invention.

Fig. 6 is a simplified diagram showing a structure of an EDI
20 deionized water producing apparatus according to another preferred embodiment of the present invention.

Fig. 7 is a simplified diagram showing another example structure of a concentrating chamber.

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DESCRIPTION OF PREFERRED EMBODIMENT

[Example structure of an EDI deionized water producing apparatus]

An example structure of an EDI deionized water producing apparatus suitable for use in a preferred embodiment of the present invention will now be described referring to Fig. 6. Between an
5 anode chamber 32b having an anode 37 and a cathode chamber 32a having a cathode 36, desalination chambers D, each of which has a side near the anode 37 separated by an anion exchange membrane 34 and a side near the cathode 36 separated by a cation exchange membrane 33 and concentrating chambers 31, each of which has a side near
10 the anode 37 separated by the cation exchange membrane 33 and a side near the cathode 36 separated by the anion exchange membrane 34 are alternately provided.

An upper portion of the desalination chamber D is filled with an anion ion exchanger A and a lower portion of the desalination
15 chamber D is filled with a mixture ion exchanger in which an anion ion exchanger and a cation ion exchanger are mixed. On the other hand, a side of the concentrating chamber 31 near the anode is separated by the cation exchange membrane 33, a side of the concentrating chamber 31 near the cathode is separated by the anion
20 exchange membrane 34, and the concentrating chamber 31 is filled with a mixture ion exchanger of an anion exchanger and a cation exchanger.

The ion exchanger to be filled in the desalination chamber D is not limited to those specifically described above, and may
25 alternatively be only an anion exchange resin, only a cation exchange

resin, or only a mixture ion exchange resin, depending on water to be treated.

In such a device, a DC current is applied between the cathode 36 and the anode 37, water to be treated is supplied from an introduction line 41 for water to be treated, and concentrate water is supplied from an introduction line 45 for concentrate water. In addition, cathode water and anode water are supplied respectively from an introduction line 47a for cathode water and an introduction line 47b for anode water.

10 The water to be treated flowing from the introduction line 41 for water to be treated flows down the desalination chamber D in which impurity ions are removed while the water to be treated passes through the filled layers of the anion exchanger A and the mixture ion exchanger M, and deionized water is obtained from an exit line 44 for deionization water.

15 The concentrate water flowing from the introduction line 45 for concentrating water moves upwards in each concentrating chamber 31 and receives within the concentrating chamber impurity ions moving through the cation exchange membrane 33 and through the anion exchange membrane 34 and impurity ions moving through the mixture ion exchanger 39. The concentrate water is then discharged from an exit line 46 for concentrating chamber as concentrated water in which impurity ions are concentrated.

25 Moreover, the cathode water flowing from the introduction line 47a for cathode water is discharged from an exit line 48a for cathode

water and the anode water flowing from the introduction line 47b for anode water is discharged from an exit line 48b for anode water.

With these operations, impurity ions within the water to be treated supplied from the introduction line 41 for water to be treated are electrically removed and deionized water from which the impurity ions are removed is obtained at the exit line 44 for deionized water. In addition, concentrated water in which impurity ions are concentrate is obtained from the exit line 46 for concentrated water.

The EDI deionized water producing apparatus may alternatively be formed in a configuration as shown in Fig. 5. A structure of a desalination chamber in this configuration is described in Japanese Patent Laid-Open Publication No. 2001-239270.

As shown in Fig. 5, in an EDI deionized water producing apparatus 10a, desalination chambers D and concentrating chambers 31 are alternately provided between an anode chamber 32b having an anode 37 and a cathode chamber 32a having a cathode 36. In the desalination chamber D, a side near the anode is demarcated by an anion exchange membrane 34 and a side near the cathode is demarcated by a cation exchange membrane 33, and the desalination chamber D comprises two small desalination chambers d_1 and d_2 separated by an intermediate ion exchange membrane 35 provided between the anion exchange membrane 34 and the cation exchange membrane 33. On the other hand, in the concentrating chamber 31, a side near the anode is separated by the cation exchange membrane 33 and a side near the cathode is separated by the anion exchange membrane 34, and the concentrating

chamber 31 is filled with a mixture ion exchanger 39 of an anion ion exchanger and a cation ion exchanger.

As shown in the lower portion of Fig. 5, a desalination chamber D_1 is formed of a first small desalination chamber d_1 and a second small desalination chamber d_2 and a desalination chamber D_2 is formed of a first small desalination chamber d_3 and a second small desalination chamber d_4 . Similarly, a desalination chamber D_3 is formed of a first small desalination chamber d_5 and a second small desalination chamber d_6 and a desalination chamber D_4 is formed of a first small desalination chamber d_7 and a second small desalination chamber d_8 .

Normally, the EDI deionized water producing apparatus 10a is operated as follows. A DC current is applied between the cathode 36 and the anode 37. Water to be treated is supplied from the introduction line 41 for water to be treated, concentrate water is supplied from the introduction line 45 for concentrate water, and cathode water and anode water are supplied respectively from the introduction line 47a for cathode water and the introduction line 47b for anode water. The water to be treated supplied from the introduction line 41 for water to be treated flows down the second small desalination chambers d_2 , d_4 , d_6 , and d_8 and impurity ions are removed while the water to be treated passes through the filled layer of ion exchanger 38. The discharge water flowing through the exit line 42 for treated water of the second small desalination chamber is introduced through an introduction line 43 for water

to be treated of the first small desalination chamber to the first small desalination chambers d_1 , d_3 , d_5 , and d_7 . The water to be treated flows down the first small desalination chambers d_1 , d_3 , d_5 , and d_7 and impurity ions are removed when the water to be treated passes
5 through the filled layer of the ion exchanger 38. Deionized water is thus obtained from the exit line 44 for deionized water.

The concentrate water flowing from the introduction line 45 for the concentrating water moves upward through each concentrating chamber 31, receives impurity ions moving through the cation exchange
10 membrane 33 and through the anion exchange membrane 34 and impurity ions moving through the ion exchanger within the concentrating chamber as will be described later, and is discharged from the exit line 46 for concentrating chamber as concentrated water in which impurity ions are concentrated.

15 The cathode water supplied from the introduction line 47a for cathode water is discharged from the exit line 48a for cathode water and the anode water supplied from the introduction line 47b for anode water is discharged from the exit line 48b for anode water.

With these operations, impurity ions within the water to be
20 treated supplied from the introduction line 41 for water to be treated are electrically removed and deionized water from which the impurity ions are removed can be obtained from the exit line 44 for deionized water. In addition, concentrate water in which impurity ions are concentrate is obtained from the exit line 46 for concentrated water.

25 In the EDI deionized water producing apparatus of the present

embodiment, by filling with an anion exchange the second small desalination chambers d_2 , d_4 , d_6 , and d_8 to which the water to be treated flows and the first small desalination chambers d_1 , d_3 , d_5 , and d_7 receiving the water exiting from the second small desalination chamber as the water to be treated with a mixture ion exchanger, it is possible to remove silica, carbonic acid, or the like in both the second and first small desalination chambers. Because of this, it is possible to sufficiently treat water to be treated which contains, in a large proportion, weak acid compositions such as silica carbonic acid which are difficult to remove. As a result, it is possible to omit provision of the decarbonator device for reducing free carbon dioxide as an upstream treatment of the EDI deionized water producing apparatus.

In the EDI deionized water producing apparatus shown in Figs. 5 and 6 described above, the concentrating chamber is filled with the mixture ion exchanger 39. The material to fill the concentrating chamber 31 is, however, not limited to the mixture ion exchanger. For example, it is also possible to employ a configuration as shown in Fig. 7 in which an anion exchanger 62 is provided on the anode side of the anion exchange membrane 34 and a water permeating material 60 having no strongly basic anion exchange group is provided between the anion exchanger 62 and the cation exchange membrane 34.

[First operation method]

In a first method of operation, in an EDI deionized water producing apparatus having, between an anode chamber having an anode

and a cathode chamber having a cathode, a desalination chamber in which a side near the anode is demarcated by an anion exchange membrane and a side near the cathode is demarcated by a cation exchange membrane and a concentrating chamber in which a side near the anode is demarcated by a cation exchange membrane and a side near the cathode is demarcated by an anion exchange membrane and which concentrating chamber is filled with an anion exchanger on the anode side of the anion exchange membrane, water containing free carbon dioxide is supplied to the concentrating chamber.

10 In the operation method according to this preferred embodiment, an apparatus as described above and shown in Figs. 5, 6, and 7 may be used as the EDI having, deionized water producing apparatus between an anode chamber having an anode and a cathode chamber having a cathode, a desalination chamber in which a side near the anode is separated by an anion exchange membrane and a side near the cathode is separated by a cation exchange membrane and a concentrating chamber in which a side near the anode is demarcated by a cation exchange membrane and a side near the cathode is demarcated by an anion exchange membrane.

20 An example of the anion exchanger includes a strongly basic anion exchanger. Examples of forms of the anion exchanger include, an anion exchange resin, an anion exchange fiber, and an organic porous anion exchanger described in Japanese Patent Laid-Open Publication No. 2002-306976. The strongly basic anion exchanger may partially include weakly basic anion exchange group. Among these

different forms, an anion exchange resin is preferred because the exchange capacity per filled volume is large, and therefore the residence time of carbonate ions is long, and time for allowing reaction with the free carbon dioxide in the concentrating water is long, which consequently result in sufficient amount of reaction to occur even with a low concentration of free carbon dioxide, and thus, inhibition of formation of scales. In addition, when the particle size of the anion exchange resin is uniform, the differential pressure across the concentrating chamber is reduced, and, thus, the use of an anionic exchange resin is desirable.

A desired salt-splitting capacity of the anion exchanger is $0.75 \text{ g CaCO}_3/\text{l} - 75 \text{ g CaCO}_3/\text{l}$ (wet resin). When the capacity is less than $0.75 \text{ g CaCO}_3/\text{l}$, the EDI system is not desirable because the residence time of carbonate ions is reduced and the time for allowing reaction with the free carbon dioxide in the concentrate water is reduced. When, on the other hand, the capacity exceeds $75 \text{ g CaCO}_3/\text{l}$, the EDI system is also not desirable because the manufacturing cost of the anion exchanger is increased. When the anion exchanger is an anion exchange resin, the anion exchanger may be of either gel type or MR type. However, because the ion selectivity with respect to ions other than hydroxide ions of the gel type exchange resin is not as strong as that of the MR type exchange resin and the electrical resistance of the gel type exchange resin in a form of salt is low, it is possible, with the gel type exchange resin, to more reliably receive carbonate ions and hydroxide

ions moving from the anion exchange membrane and to move these ions to the side near the anode. Therefore, the gel type exchange resin is preferred over the MR type exchange resin.

The concentrating chamber may be of a form in which the entire
5 concentrating chamber is filled with an anion exchanger alone. However, in this form, because the anion exchange groups exist continuously in the concentrating chamber, almost all of the bicarbonate ions within the anion exchanger move to the side of the cation exchange membrane, are concentrated, and are discharged
10 into the concentrate water. As a result, the concentration of free carbon dioxide near the cation exchange membrane becomes high and degradation of quality of the treated water tends to occur. In view of this, it is desirable to employ a form of a concentrating chamber in which an anion exchanger is provided on the anode side of the
15 anion exchange membrane and a water permeating material having no strong basic anion group is provided between the anion exchanger and the cation exchange membrane, because in this form, the anion exchanger does not come in contact with the cation exchange membrane in the concentrating chamber, the concentration of free carbon
20 dioxide near the cation exchange membrane is not increased, and degradation of quality of the treated water can be prevented. Examples of the anion exchanger to be provided on the anode side of the anion exchange membrane include those anion exchangers described above.

25 The water permeating material having no strong basic anion

exchange group which is provided between the anion exchanger and the cation exchange membrane is used to secure flow pathes for the concentrate water and to prevent contact between the anion exchange group and the cation exchange membrane. Therefore, the water permeating material having no strong anion exchange group may be either a conductive water permeating material or non-conductive water permeating material. When a conductive water permeating material is to be used, it is possible to use water permeating material having an exchange group other than the strongly basic anion exchange group such as a weakly basic anion exchange group, a weakly acidic cation exchange group, and a strongly acidic cation exchange group. Examples of a material having a weakly acidic cation exchange group or a strong acidic cation exchange group include, for example, a cation exchange fiber and a cation exchange resin. In particular, when a cation exchange resin is to be used, it is desirable to use a cation exchange resin having a degree of cross-linkage of 4% or less as such a resin allows for reduction of selectivity for divalent ions such as calcium ion, magnesium ion, and the like, increase in selectivity of hydrogen ion, and reduction of opportunity of contact between hardness components and carbonate ions. Examples of non-conductive water permeating material include, for example, a mesh-shaped structure, a nonwoven fabric, a woven fabric, and other porous materials. Of these, a mesh-shaped structure is desirable as the selection of mesh size is easy, water permeability is high, and it does not tends to cause an increase in differential

pressure in the concentrating chamber.

The thickness of the concentrating chamber is preferably between 0.5 mm and 6 mm, and is more preferably between 1.0 mm and 3 mm. When the thickness of the concentrating chamber is less than 5 0.5 mm, even when the concentrating chamber is filled with an ion exchanger, the advantage of inhibiting formation of scales is less effectively obtained and the differential pressure across the chamber water tends to increase. When, on the other hand, the thickness exceeds 6 mm, the electrical resistance is increased and 10 the power consumption is increased. Although the thickness of the water permeating material having no strong basic anion exchanger is not limited, it is preferable that the thickness is between 0.1 mm and 2.0 mm, and it is more preferable that the thickness is between 0.2 mm and 1.0 mm. When the thickness of the water permeating material 15 is less than 0.1 mm, a distance between a portion in which the free carbon dioxide is generated and the cation exchange membrane is reduced, resulting in a high concentration of free carbon dioxide near the cation exchange membrane. When, on the other hand, the thickness exceeds 2.0 mm, the electrical resistance of the water 20 permeating material is increased and the power consumption is increased. The concentrating chamber having this structure is a two-layered structure of an anion exchanger and a water permeating material having no strong basic anion exchange group, but it is only required that the anion exchanger and the cation exchange 25 membrane be substantially not in contact with each other and the

anion exchanger and the cation exchange membrane may partially contact each other to an extent which does not hamper the advantages of the present invention.

When the anion exchanger to be filled in the anode side of the anion exchange membrane is an exchange resin in the form of beads, it is desirable to select a water permeating material having a finer mesh size than the effective size of the ion exchange resin beads because such sizing allows for reliable prevention of contact between the anion exchange resin and the cation exchange membrane. In addition, when the anion exchanger is an ion exchange resin in the form of beads, it is desirable to use an ion exchange resin having a relatively large average bead size and uniform distribution of bead size, because such a allows for a larger effective size of the ion exchange resin, and consequently, selection of a coarser mesh for the water permeating material, which result in a higher water permeability without an increase in differential pressure. The effective size of the ion exchange resin beads is defined by the mesh size of a screen which allows 10 volume% of the resin to pass through.

Water including free carbon dioxide which is used in the first method of operation is water having a concentration of free carbon dioxide of 0.5 mg CO₂/l - 200 mg CO₂/l, and preferably having a concentration of free carbon dioxide of 2 mg CO₂/l - 150 mg CO₂/l. When the concentration of free carbon dioxide is less than 0.5 mg CO₂/l, the advantage of inhibition of formation of scales is hampered

and when the concentration of free carbon dioxide exceeds $200 \text{ mgCO}_2/\text{l}$, the amount of free carbon dioxide which diffuses into an adjacent desalination chamber through the cation exchange membrane is increased, resulting in degradation of the quality of the treated water. Specific examples of water including free carbon dioxide include permeate water of a reverse osmosis membrane in which tap water or industrial water is roughly desalinated. Although a reverse osmosis membrane removes ion compositions, it allows most of the gas compositions to pass through. As such, a high concentration of free carbon dioxide which has permeated thorough the reverse osmosis membrane as dissolved carbon dioxide gas remains in the permeate water. Therefore, it is possible to use the permeate water of the reverse osmosis membrane as the supply water of the concentrating chamber thereby doing without adding any chemical to the water. The permeate water of the reverse osmosis membrane may also be used as the water to be fed to the desalination chamber of the EDI deionized water producing apparatus.

In a system in which a decarbonator is provided between the reverse osmosis membrane device and the EDI deionized water producing apparatus, it is desirable to employ a configuration in which the treated water of the decarbonator is used as the water to be supplied to the desalination chamber of the EDI unit (water to be treated by the EDI unit) and the permeate water of reverse osmosis membrane which is the water to be treated by the decarbonator device is also used as the water to be supplied to the concentrating chamber of

the EDI unit, as such a configuration allows for supply, to the concentrating chamber, of water having free carbon dioxide in an amount necessary for inhibiting the formation of scale while reducing the concentration of free carbon dioxide which is a load on the desalination chamber. In addition, when the treated water of the decarbonator device is used both as the water to be supplied to the desalination chamber and as the water to be supplied to the concentrating chamber, it is desirable to circulate a portion of the exiting water of the concentrating chamber, mix the circulating water with the water having low concentration of free carbon dioxide, and supply to the concentrating chamber, as such a configuration allows for the exiting water of the concentrating chamber to have concentrated free carbon dioxide which is contained in the water to be treated, and consequently, allows for the use of the exiting water of the concentrating chamber as supply water to the concentrating chamber as water having high concentration of free carbon dioxide. The decarbonator device is not limited in its type, and, for example, a membrane type degasifier may be used.

[Second operation method]

In a second method of operation, in an EDI deionized water producing apparatus comprising, between an anode chamber having an anode and a cathode chamber having a cathode, a desalination chamber in which a side near the anode is demarcated by an anion exchange membrane and a side near the cathode is demarcated by a cation exchange membrane, and a concentrating chamber in which a

side near the anode is demarcated by a cation exchange membrane and a side near the cathode is demarcated by an anion exchange membrane and which is filled with a mixture ion exchanger of an anion exchanger and a cation exchanger, water containing free carbon dioxide is
5 supplied to the concentrating chamber.

In the description of the second operation method, elements identical to those in the first operation method will be omitted and the differing portions will primarily be described. Specifically, the second operation method of the EDI unit differs
10 from the first operation method of the EDI unit in that, in the second operation method, the material to fill the concentrating chamber is a mixture ion exchanger of an anion exchanger and a cation exchanger. According to the present embodiment, because a cation exchanger for supplying hydrogen ions is mixed with the anion
15 exchanger and the mixture is filled, the bicarbonate ions moving through the anion exchanger is discharged into the concentrate water as free carbon dioxide before the hydrogen-carbonate ions reach the cation exchange membrane by an action of the bicarbonate from the cation exchanger. With this structure, it is possible to prevent
20 an increase in the concentration of free carbon dioxide near the cation exchange membrane and the adverse influence on the quality of the treated water is alleviated.

As an anion exchanger in the mixture ion exchanger, it is possible to use anion exchangers similar to those described above.
25 As the cation exchanger, any cation exchanger having the capability

to supply hydrogen ions may be used, and examples of the cation exchanger include, for example, a strongly acidic cation exchanger, a weakly acidic cation exchanger, and a mixture cation exchanger of a strongly acidic cation exchanger and a weakly acidic cation exchanger. Examples of forms of the cation exchanger include a cation exchange resin, a cation exchange fiber, and an organic porous cation exchanger described in Japanese Patent Laid-Open Publication No. 2002-306976. It is desirable to use a mixture ion exchange resin of an anion exchange resin and a cation exchange resin as the mixture ion exchanger.

Examples of the mixture form of the mixture ion exchanger include, for example, a uniform mixture of an anion exchanger and a cation exchanger and a mixture ion exchanger in which the percentage of cation exchanger increases from the side near the anion exchange membrane toward the cation exchange membrane. Of these, the mixture ion exchanger in which the percentage of cation exchanger increases from the side near the anion exchange membrane toward the cation exchange membrane is more preferable. With such a configuration, the percentage of the anion exchanger (anion exchange resin) at the side of the cation exchange membrane is low, which allows for reliable reduction of concentration of free carbon dioxide near the cation exchange membrane. Examples of the form in which the percentage of the cation exchanger increases from the side near the anion exchange membrane toward the cation exchange membrane include, for example, a form in which the percentage of the cation exchanger is progressively

increased from the side near the anion exchange membrane toward the cation exchange membrane and a layered structure form in which, for example, a layer of an anion exchanger and a layer of a mixture material of an anion exchanger and a cation exchanger are placed
5 in that order from the side near the anion exchange membrane toward the cation exchange membrane. In the case of a mixture ion exchange resin, it is preferable to use a mixture ion exchange resin with uniform particle size as such a configuration reduces the differential pressure across the concentrating chamber.

10 The percentage of the cation exchange resin within the mixture ion exchange resin is not limited, but is preferably 10% - 90% in volume, and more preferably 20% to 50% in volume. When the percentage of the cation exchange resin (in volume) is less than 10%, it is not possible to prevent the increase in the concentration of free
15 carbon dioxide near the cation exchange membrane and when, on the other hand, the percentage exceeds 90%, the advantage of inhibition of formation of scales cannot be obtained, and thus, both of these percentage are not preferred. It is preferable that the degree of cross-linkage of the cation exchange resin is 4% or less, as such
20 a cross-linkage allows for a reduction of selectivity of divalent ions such as calcium ions and magnesium ions and an increase in selectivity of hydrogen ions.

[Example structure 1]

An EDI deionized water producing apparatus of a first example
25 structure will now be described referring to Fig. 1. A decarbonator

20 is placed upstream of an EDI unit 10 having a desalination chamber 12 and a concentrating chamber 11. An exit pipe 14 for treated water of the decarbonator 20 and an introduction pipe 15 for water to be treated by the EDI unit are connected and an introduction pipe 13 for water to be treated by the decarbonator 20 and an introduction pipe 16 for concentrate water of the EDI unit 10 are connected. Reference numeral 17 represents an exit pipe for concentrate water and reference numeral 18 represents an exit pipe for deionized water. The treated water of the decarbonator 20 is supplied to the introduction pipe 15 for water to be treated by the EDI 10 unit and the water to be treated by the decarbonator 20 is supplied to the introduction pipe 16 for concentrate water of the EDI unit 10. As the decarbonator 20, any of the known structure may be used such as, for example, a membrane degasifier and a decarbonator column.

Therefore, the permeate water of reverse osmosis membrane which is the water to be treated is directly supplied to the concentrating chamber 11 and is also supplied to the desalination chamber 12 after carbon dioxide is removed in the decarbonator device 20.

The treated water of the decarbonator 20 is supplied to the introduction pipe 15 for water to be treated by the EDI unit 10. In addition to the form shown in Fig. 1, the form of introduction of the water to be treated by the decarbonator 20 to the introduction pipe 16 for concentrate water of the EDI unit 10 may alternatively be one of the forms shown in Figs. 2 and 3.

In the system of Fig. 2, a buffer tank 29 for facilitating

adjustment of an amount of flow of the concentrate water is provided upstream of the decarbonator 20. The upstream side of the introduction pipe 16 for concentrate water and the upstream side of the introduction pipe 13 for water to be treated by the decarbonator 20 are connected to the buffer tank 29. Thus, the water to be treated is supplied from the buffer tank 29 directly to the concentrating chamber 11 and to the desalination chamber 12 after the removal of carbon dioxide by in the decarbonator 20.

In the system of Fig. 3, the buffer tank 29 is provided midway along the introduction pipe 16 for concentrate water of the EDI unit 10 and a return pipe 171 is provided connecting the exiting pipe 17 for concentrate water and the buffer tank 29.

With this system also, the permeate water of the reverse osmosis membrane is supplied to the desalination chamber 12 after carbon dioxide is removed in the decarbonator 20. On the other hand, in the buffer tank 29, the permeate water of reverse osmosis membrane and the concentrated water are mixed and then supplied to the concentrating chamber 11.

As the EDI unit 10 in any of the systems shown in Figs. 1 through 3, a first EDI unit in which cation exchange membrane and anion exchange membrane are alternately provided between an anode chamber having an anode and a cathode chamber having a cathode and which has a desalination chamber in which a side near the anode is demarcated by an anion exchange membrane and a side near the cathode is demarcated by a cation exchange membrane and a concentrating

chamber in which a side near the anode is demarcated by a cation exchange membrane, a side near the cathode is demarcated by an anion exchange membrane, and the anode side of the anion exchange membrane is filled with an anion exchanger may be used or a second EDI unit
5 having a structure similar to the first EDI unit except that the anode side of the anion exchange membrane in the concentrating chamber is filled with a mixture ion exchanger of a cation exchanger and an anion exchanger instead of the anion exchanger may be used.

As the anion exchanger and the cation exchanger in the second
10 EDI unit, materials similar to those described above regarding the operation methods may be used. Examples of forms of mixture of the mixture ion exchanger include, for example, a uniform mixture of an anion exchanger and a cation exchanger and a mixture ion exchanger in which the percentage of the cation exchanger increases from the
15 side near the anion exchange membrane toward the cation exchange membrane. Of these, it is more desirable to use the mixture ion exchange resin in which the percentage of the cation exchange resin increases from the side near the anion exchange membrane toward the cation exchange membrane. With such a structure, because the
20 percentage of the anion exchanger (anion exchange resin) at the side of the cation exchange membrane is low, and thus, it is possible to reliably reduce the concentration of free carbon dioxide near the cation exchange membrane. The form in which the percentage of the cation exchanger increases from the side near the anion exchange
25 membrane toward the cation exchange membrane, the percentage of

cation exchange resin within the mixture ion exchange resin, and the degree of cross-linkage of the cation exchange resin may be similar to those described above regarding the operation methods.

It is also preferable to employ a structure of the EDI unit with small desalination chambers as shown in Fig. 5. It is possible to use the EDI unit having the structure as shown in Fig. 5 as first or second EDI unit described above.

In the EDI of the first example structure shown in Figs. 1 through 3, the water to be treated which is supplied to the desalination chamber 12 is treated water of the decarbonator 20, and thus, the carbon dioxide is removed. On the other hand, no carbon dioxide is removed from the water which is supplied to the concentrating chamber 11. In this embodiment, because the water is treated (permeate) water of a reverse osmosis membrane, it is possible to supply, to the concentrating chamber 11, water having free carbon dioxide at a concentration necessary for inhibiting formation of scales while reducing the concentration of free carbon dioxide which is a load on the desalination chamber 12.

[Example structure 2]

An EDI unit according to a second example structure of the present invention is a device in which cation exchange membranes and anion exchange membranes are alternately provided between an anode chamber having an anode and a cathode chamber having a cathode and which has a desalination chamber in which a side near the anode is demarcated by an anion exchange membrane and a side near the

cathode is demarcated by a cation exchange membrane, and a concentrating chamber in which a side near the anode is demarcated by a cation exchange membrane, a side near the cathode is demarcated by an anion exchange membrane, an anion exchanger is provided on
5 the anode side of the anion exchange membrane, and a water permeating material having no strong basic anion exchange group is provided between the anion exchanger and the cation exchange membrane.

The water to be treated by the EDI unit of the second example structure is not limited, and may be, for example, treated water
10 of a decarbonator. The water to be supplied to the concentrating chamber is not limited as long as the water contains free carbon dioxide. As the anion exchanger and the water permeating material, structures similar to those described above regarding the operation methods may be used.

15 In the first and second example structures, the structure of the desalination chamber is not limited, and any of the structures as shown in, for example, Figs. 5 and 6 may be used.

[Example structure 3]

An EDI unit of a third example structure will now be described
20 referring to Fig. 4. Fig. 4 is a schematic diagram showing an EDI unit in the third example structure. In Fig. 4, elements identical to those shown in Fig. 1 are assigned the same reference numerals and will not be described again, and the difference will primarily be described. In the structure of Fig. 4, no decarbonator upstream
25 of an EDI unit 10a having a desalination chamber 12a and a

concentrating chamber 11a is provided, a reverse osmosis membrane device 30 is provided, an exit pipe 19 for permeate water of the reverse osmosis membrane device 30 and an introduction pipe 192 for water to be treated by the EDI unit 10a are connected, and the introduction pipe 19 for permeated water is branched to form a supply pipe 191 of concentrate water.

In this third example structure, a device having a structure as shown in Fig. 5 and described above is used as the EDI unit. An anion exchanger is filled into second small desalination chambers d_2 , d_4 , d_6 , and d_8 into which water to be treated flows and a mixture ion exchanger is filled into first small desalination chambers d_1 , d_3 , d_5 , and d_7 having the exit water of the second small desalination chamber as the water to be treated. In this configuration, silica, carbonic acid, and the like can be removed both in the second small desalination chamber and the first small desalination chamber. Because of this, it is possible to sufficiently treat water to be treated having a large amount of silica and weak acidic compositions such as carbonic acid which is particularly difficult to remove among anion compositions. It is possible to omit the decarbonator for reducing free carbon dioxide as a pretreatment of the EDI unit.

[Examples]

Example 1

An EDI deionized water producing apparatus in which four deionization modules (eight small desalination chambers) are provided in parallel similar to the structure shown in Fig. 5 was

used under the device specification and operation conditions as described below. Permeate water of a reverse osmosis membrane treating industrial water was used as water to be treated, with the hardness of the water to be treated being $1000 \mu\text{g CaCO}_3/\text{l}$ and the concentration of free carbon dioxide being $4 \text{mg CO}_2/\text{l}$. In addition, a portion of the water to be treated was used directly as the concentrate water and electrode water. The operation time was 4000 hours and presence of scales in the concentrating chamber after 4000 hours was observed. Resistivity of the treated water and operation conditions after the operation of 4000 hour period are shown in Table 1.

[Operation conditions]

EDI deionized water producing apparatus: Prototype EDI unit;
Intermediate ion exchange membrane: Anion exchange membrane;
15 First small desalination chamber: Width 100 mm, Height 300 mm, thickness 4 mm;
Ion exchange resin filled into first small desalination chambers:
Mixture ion exchange resin of anion exchange resin (A) and cation exchange resin (C) (with mixture ratio in volume of A:C = 1:1);
20 Second small desalination chamber: Width 100 mm, Height 300 mm, thickness 8 mm;
Ion exchange resin filled into second small desalination chambers:
Anion exchange resin;
Concentrating chamber: Width 100 mm, Height 300 mm, thickness 2
25 mm;

Ion exchange resin filled into concentrating chambers: Gel type strongly basic anion exchange resin (Amberlite IRA-402BL)

Rate of flow in overall device: 0.1 m³/h

5 Example 2

An operation similar to that for the Example 1 was performed except that a mixture ion exchange resin of a cation exchange resin (Amberlyst30W with a degree of cross-linkage of 4%) and a gel type strong basic anion exchange resin (Amberlite IRA-402BL) (with a
10 mixture ratio of A:C = 1:1 in volume) was filled in the concentrating chamber instead of the gel type strong basic anion exchange resin (Amberlite IRA-402BL). Resistivity of the treated water after 4000 hours of operation and operational conditions are shown in Table 1.

15

Example 3

An operation similar to that for the Example 1 was performed except that a gel type strong basic anion exchange resin (Amberlite IRA-402BL having an effective size of 0.45 mm) was filled in the
20 anode side of the anion exchange membrane to a thickness of 1.7 mm instead of the gel type strong basic anion exchange resin (Amberlite IRA-402BL) filled in the concentrating chamber and a mesh-shaped structure having a mesh size of 60 meshes is filled between the gel type strongly basic anion exchange resin and the cation exchange
25 membrane to a thickness of 0.3 mm. Resistivity of the treated water

after 4000 hours of operation and operational conditions are shown in Table 1.

Comparative Example 1

5 An operation similar to that for the Example 1 was performed except that a mesh-shaped structure having a mesh size of 12 meshes and a thickness of 1 mm was filled instead of the gel type strong basic anion exchange resin (IRA-402BL) filled into the concentrating chamber and the thickness of the concentrating chamber was set to
10 1 mm. In the Comparative Example 1, because the voltage reached 250 V after 100 hours of operation, the operation of the apparatus was stopped and presence of scales within the concentrating chamber was observed. Resistivity of the treated water after 100 hours of operation and operational conditions are shown in Table 1.

15

Comparative Example 2

 An operation similar to that for the Example 1 was performed except that permeate water of reverse osmosis membrane treating industrial water removed from which carbon dioxide was through a
20 membrane type degasifier was used instead of permeate water of reverse osmosis membrane treating industrial water. In the Comparative Example 2, because the voltage reached 250 V after 150 hours of operation, the operation of the apparatus was stopped and presence of scales within the concentrating chamber was observed.
25 Resistivity of the treated water after 150 hours of operation and

operational conditions are shown in Table 1.

[Table 1]

	EXAMPLE 1	EXAMPLE 2	EXAMPLE 3	COMPARATIVE EXAMPLE 1	COMPARATIVE EXAMPLE 2
APPLIED VOLATAGE (V)	75	80	80	250	250
CURRENT (A)	0.6	0.6	0.6	0.6	0.6
RESISTIVITY OF TREATED WATER (M Ω · cm)	17.0	17.5	17.9	10.5	11.0
PRESENCE OF SCALES	NOT OBSERVED	NOT OBSERVED	NOT OBSERVED	OBSERVED	OVSERVED

As described, according to the present embodiment, it is possible to solve the problem of formation of scales by controlling conditions of water to be supplied to the concentrating chamber of the EDI unit and to achieve a stable operation without noticeable amount of formation of scales within the concentration chamber even in a continuous treatment for a long period of time of water to be treated having a high concentration of hardness components. In addition, the conductivity within the concentrating chamber can be stabilized, uniform current density can be obtained in the entire desalination chamber from the entrance side to the exit side, and power consumption can be reduced.

What is claimed is:

1. A method for operating an electrodeionization deionized water
5 producing apparatus comprising, between an anode chamber having an
anode and a cathode chamber having a cathode, a desalination
chamber in which a side near the anode is demarcated by an anion
exchange membrane and a side near the cathode is demarcated by a
cation exchange membrane and a concentrating chamber in which a
10 side near the anode is demarcated by a cation exchange membrane, a
side near the cathode is demarcated by an anion exchange membrane,
and the anode side of the anion exchange membrane is filled with an
anion exchanger, the method comprising the step of:

supplying water containing free carbon dioxide to the
15 concentrating chamber.

2. A method for operating an electrodeionization deionized water
producing apparatus comprising, between an anode chamber having an
anode and a cathode chamber having a cathode, a desalination
20 chamber in which a side near the anode is demarcated by an anion
exchange membrane and a side near the cathode is demarcated by a
cation exchange membrane and a concentrating chamber in which a
side near the anode is demarcated by a cation exchange membrane and
a side near the cathode is demarcated by an anion exchange membrane
25 and which concentrating chamber is filled with a mixture ion
exchanger of an anion exchanger and a cation exchanger,

wherein the mixture ion exchanger filled into the concentrating chamber is a mixture ion exchanger in which a percentage of the cation exchanger increases from the side near the anion exchange membrane toward the side near the cation exchange
5 membrane,

the method comprising the step of:

supplying water containing free carbon dioxide to the concentrating chamber.

10 3. A method for operating an electrodeionization deionized water producing apparatus according to Claim 1, wherein

in the concentrating chamber, an anion exchanger is provided on the anode side of the anion exchange membrane and a water permeating material having no strongly by basic anion exchange
15 group is provided between the anion exchanger and the cation exchange membrane.

4. A method for operating an electrodeionization deionized water producing apparatus according to any one of Claims 1 through 3,

20 wherein

the water to be supplied to the concentrating chamber is water having a concentration of free carbon dioxide of 0.5 mg-CO₂/l - 200 mg-CO₂/l.

25 5. An electrodeionization deionized water producing system having an electrodeionization deionized water producing apparatus, wherein

the electrodeionization deionized water producing apparatus comprises, between an anode chamber having an anode and a cathode chamber having a cathode, a desalination chamber in which a side near the anode is demarcated by an anion exchange membrane and a side near the cathode is demarcated by a cation exchange membrane and a concentrating chamber in which a side near the anode is demarcated by a cation exchange membrane, a side near the cathode is demarcated by an anion exchange membrane, and the anode side of the anion exchange membrane is filled with an anion exchanger;

a decarbonator is provided upstream of the electrodeionization deionized water producing apparatus;

treated water of the decarbonator is supplied to the desalination chamber of the electrodeionization deionized water producing apparatus; and

water to be treated by the decarbonator is supplied, without being treated by the decarbonator, to the concentrating chamber of the electrodeionization deionized water producing apparatus.

6. An electrodeionization deionized water producing system having an electrodeionization water producing apparatus, wherein

the electrodeionization deionized water producing apparatus comprises, between an anode chamber having an anode and a cathode chamber having a cathode, a desalination chamber in which a side near the anode is demarcated by an anion exchange membrane and a side near the cathode is demarcated by a cation exchange membrane, and a concentrating chamber in which a side near the anode is

demarcated by a cation exchange membrane and a side near the cathode is demarcated by an anion exchange membrane and which concentrating chamber is filled with a mixture ion exchanger of an anion exchanger and a cation exchanger, wherein

5 the mixture ion exchanger in the concentrating chamber is a mixture ion exchanger in which a percentage of the cation exchanger increases from the side near the anion exchange membrane toward the side near the cation exchange membrane;

10 a decarbonator is provided upstream of the electrodeionization deionized water producing apparatus;

 treated water of the decarbonator is supplied to the desalination chamber of the electrodeionization water producing apparatus; and

15 water to be treated of the decarbonator is supplied, without being treated by decarbonator, to the concentrating chamber of the electrodeionization deionized water producing apparatus.

7. An electrodeionization deionized water producing apparatus comprising, between an anode chamber having an anode and a cathode chamber having a cathode,

20

 a desalination chamber in which a side near the anode is demarcated by an anion exchange membrane and a side near the cathode is demarcated by a cation exchange membrane; and

25 a concentrating chamber in which a side near the anode is demarcated by a cation exchange membrane, a side near the cathode is demarcated by an anion exchange membrane, an anion exchanger is

provided on the anode side of the anion exchange membrane, and a water permeating material having no strongly basic anion exchange group is provided between the anion exchanger and the cation exchange membrane.

5

8. An electrodeionization deionized water producing apparatus, comprising, between an anode chamber having an anode and a cathode chamber having a cathode:

10 a desalination chamber in which a side near the anode is demarcated by an anion exchange membrane and a side near the cathode is demarcated by a cation exchange membrane and which desalination chamber has two small desalination chambers separated by an intermediate ion exchange membrane provided between the anion exchange membrane and the cation exchange membrane; and

15 a concentrating chamber in which a side near the anode is demarcated by a cation exchange membrane and a side near the cathode is demarcated by an anion exchange membrane and which concentrating chamber is filled with a mixture ion exchanger of an anion exchanger and a cation exchanger, wherein

20 the mixture ion exchanger in the concentrating chamber is a mixture ion exchanger in which a percentage of the cation exchanger increases from the side near the anion exchange membrane toward the side near the cation exchange membrane; wherein

25 an upstream decarbonator is omitted and permeate water of a reverse osmosis membrane device is directly used as water to be treated and water to be supplied to the concentrating chamber.

9. An electrodeionization deionized water producing apparatus comprising, between an anode chamber having an anode and a cathode chamber having a cathode:

5 a desalination chamber in which a side near the anode is demarcated by an anion exchange membrane and a side near the cathode is demarcated by a cation exchange membrane and which desalination chamber has two small desalination chambers separated by an intermediate ion exchange membrane provided between the anion
10 exchange membrane and the cation exchange membrane; and

a concentrating chamber in which a side near the anode is demarcated by a cation exchange membrane, a side near the cathode is demarcated by an anion exchange membrane, the anode side of the anion exchange membrane is filled with an anion exchanger, and a
15 water permeating material having no strongly basic anion exchange group is provided between the anion exchanger and the cation exchange membrane; wherein

an upstream decarbonator is omitted and permeate water of a reverse osmosis membrane device is directly used as water to be
20 treated and water to be supplied to the concentrating chamber.