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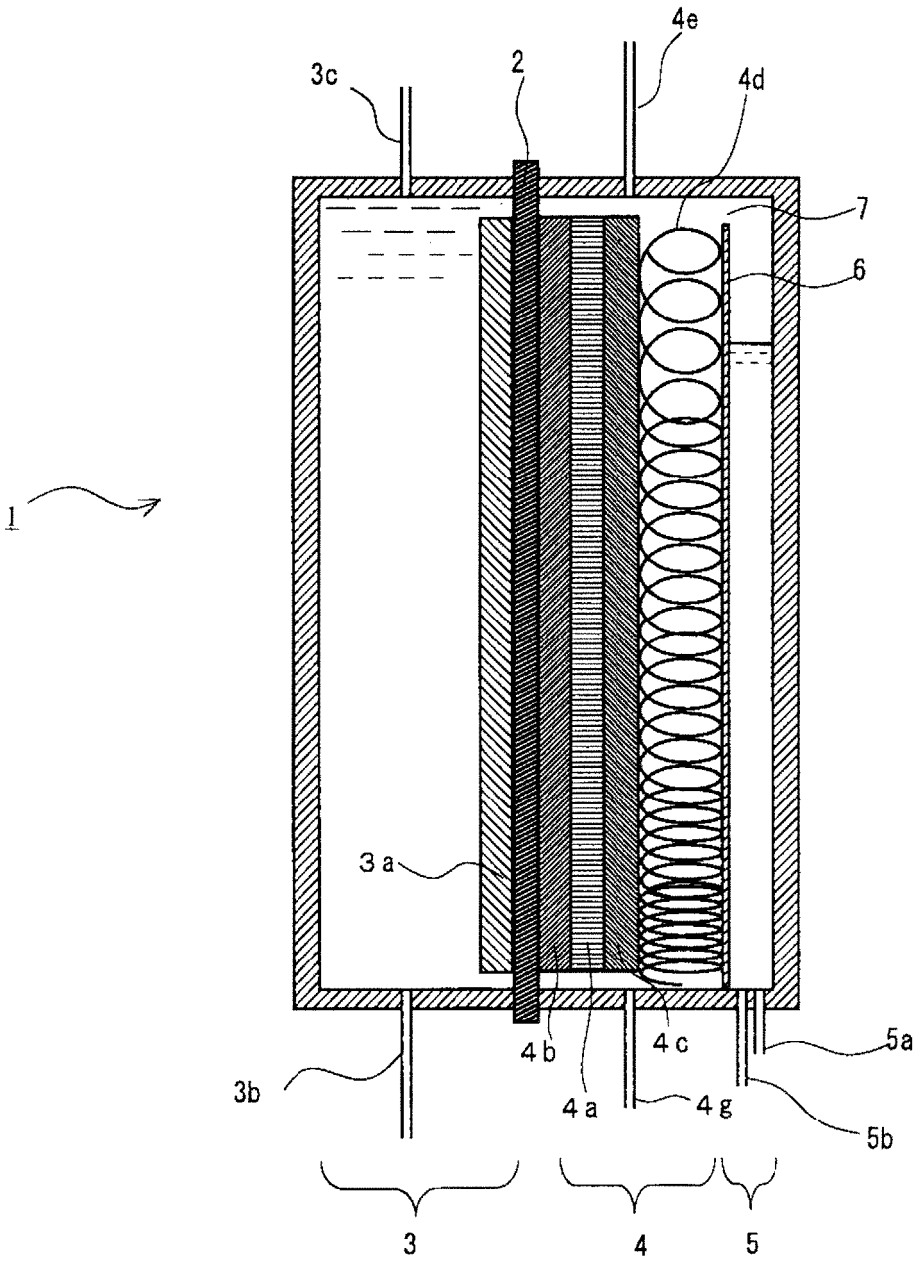
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(54) METHOD FOR MANUFACTURING SODIUM HYDROXIDE AND/OR CHLORINE AND 2 CHAMBER TYPE SALTWATER ELECTROLYTIC CELL

(57) Provided is a method for producing sodium hydroxide and/or chlorine with a two-chamber type method of an oxygen cathode method in such a way that water is supplied to a cathode chamber and overheating of an electrolytic cell is suppressed without extra energy. The present invention is the method for producing sodium hydroxide and/or chlorine by electrolyzing saltwater, using a two-chamber type electrolytic cell for saltwater having one or more unit cells equipped with an anode chamber including an anode, a cathode chamber including a gas-diffusion cathode, and an ion exchange membrane sandwiched by the anode chamber and the cathode chamber, and characterized by each of the unit cells further having a humidifying chamber generating humidified oxygen-containing gas for supplying to the cathode, and the humidifying chamber being adjoined to and in heat exchange relation with the anode chamber or the cathode chamber in one of the unit cells or in another of the unit cells adjacent to the one of the unit cells, and water vapor generation with heat from the anode chamber or the cathode chamber.

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FIG. 1



Description

TECHNICAL FIELD

[0001] The present invention relates to a method for producing sodium hydroxide and/or chlorine, and a two-chamber type electrolytic cell for saltwater.

BACKGROUND ART

[0002] Sodium hydrate and chlorine are essential as industrial materials. They have conventionally been produced by a method using an ion exchange membrane electrolytic cell to electrolyze saltwater, in which a metal electrode is used as a cathode and the saltwater is electrolyzed according to the reaction given by the following equation (1).

$$2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH + H_2 \quad (1)$$

[0003] However, since the electrolysis of saltwater according to the above equation (1) requires huge amounts of electric power, a method in which a gas-diffusion electrode is used as a cathode to reduce oxygen (hereinafter, referred to as oxygen cathode method) has been addressed in hope of significant energy saving in recent years. In the oxygen cathode method, a reaction at the anode is oxidation of chlorine ion, which is the same as in the conventional method, and as a whole, the reaction is given by the following equation (2).

$$2NaCl + 1/2O_2 + H_2O \rightarrow Cl_2 + 2NaOH \quad (2)$$

[0004] In the oxygen cathode method, a three-chamber type method, in which an electrolytic cell is divided into an anode chamber, a catholyte chamber, and a cathode gas chamber, has been employed. However, in recent years, as described in Patent Document 1, for example, a two-chamber type method has been investigated, in which an electrolytic cell is divided into an anode chamber and a cathode gas chamber by making an anode, an ion exchange membrane, and a gas-diffusion cathode attached firmly to each other to eliminate a catholyte chamber substantially. As shown in the above chemical equations, water is required for electrolyzing saltwater, and at the same time, water is also required for keeping the concentration of the generated sodium hydroxide from being too high. In the three-chamber type method, the cathode chamber has a liquid chamber to circulate aqueous sodium hydroxide, from which sufficient water is supplied. On the other hand, in the two-chamber type method, since the cathode chamber does not have a liquid chamber, water is supplied through the ion exchange membrane from the anode chamber as electro-osmosis water, which is not sufficient, and water is needed to be supplied to the cathode in some way. The Patent Document 1 discloses that the shortage of water is compensated by supplying water through the gas chamber, and specifically discloses that water is heated beforehand to 90°C and then introduced through an inlet for oxygen gas. Patent Document 2 also discloses that humidified oxygen-containing gas is supplied to the cathode chamber, and specifically discloses that the humidified oxygen-containing gas has been prepared by bubbling oxygen into water heated to 80°C and then is introduced to the cathode chamber.

RELATED ART DOCUMENTS

PATENT DOCUMENTS

[0005]

Patent Document 1: JP-A-2001-3188
Patent Document 2: JP-A-H11-152591

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0006] However, the method for supplying water disclosed in the Patent Document 1 and 2 requires energy to heat water to 80°C or 90°C. In addition, in the method disclosed in the Patent Document 1, when the temperature of the electrolytic cell becomes too high, the anolyte temperature is decreased by circulating the anolyte in an external heat exchanger and using cooling water and the like, which further requires energy for preparing the cooling water.

[0007] Considering the above, the purpose of the present invention is to offer a method capable of efficiently producing

sodium hydroxide and/or chlorine in such a way that water is supplied to the cathode chamber and overheating of the electrolytic cell is suppressed without extra energy other than the energy for electrolytic reaction.

MEANS FOR SOLVING THE PROBLEMS

[0008] The present invention includes the following:

[1] A method for producing sodium hydroxide and/or chlorine by electrolyzing saltwater, comprising using a two-chamber type electrolytic cell for saltwater comprising one or more unit cells equipped with an anode chamber including an anode, a cathode chamber including a gas-diffusion cathode, and an ion exchange membrane sandwiched by the anode chamber and the cathode chamber, supplying saltwater to the anode chamber, and supplying humidified oxygen-containing gas to the cathode chamber, wherein each of the unit cells further comprises a humidifying chamber generating the humidified oxygen-containing gas that is to be supplied to the cathode chamber, the humidifying chamber is adjoined to and in heat exchange relation with the anode chamber or the cathode chamber in one of the unit cells, or the anode chamber or the cathode chamber in another of the unit cells adjacent to the one of the unit cells, and the oxygen-containing gas is humidified by generating water vapor with heat from the anode chamber or the cathode chamber.

[2] The method according to [1], wherein the humidifying chamber is adjoined to the cathode chamber, and the humidified oxygen-containing gas generated in the humidifying chamber is supplied from the humidifying chamber to the cathode chamber through at least one opening located at a partition between the humidifying chamber and the cathode chamber.

[3] The method according to [2], wherein the at least one opening located at the partition between the humidifying chamber and the cathode chamber comprises a single opening.

[4] The method according to [2], wherein the at least one opening located at the partition between the humidifying chamber and the cathode chamber comprises a plurality of openings.

[5] The method according to [1], wherein the humidified oxygen-containing gas generated in the humidifying chamber is supplied from the humidifying chamber to the cathode chamber through at least one flow path located outside the humidifying chamber and the cathode chamber.

[6] The method according to [5], wherein the at least one flow path located outside the humidifying chamber and the cathode chamber comprises a single flow path.

[7] The method according to [5], wherein the at least one flow path located outside the humidifying chamber and the cathode chamber comprises a plurality of flow paths.

[8] The method according to any one of [1] to [7], wherein the unit cells are connected with each other in the electrolytic cell, and the unit cells are arranged such that the sequence of the anode chamber, the cathode chamber, and the humidifying chamber is repeated.

[9] A two-chamber type electrolytic cell for saltwater, comprising one or more unit cells equipped with an anode chamber, a cathode chamber, and an ion exchange membrane sandwiched by the anode chamber and the cathode chamber, wherein the anode chamber includes an anode, and is equipped with an inlet for saltwater as a starting material, an outlet for electrolyzed saltwater, and an outlet for chlorine, the cathode chamber includes a gas-diffusion cathode, and is equipped with an inlet for humidified oxygen-containing gas and an outlet for electrolytic reactant, each of the unit cells further comprises a humidifying chamber generating oxygen-containing gas that is to be supplied to the cathode chamber, and the humidifying chamber is adjoined to and in heat exchange relation with the anode chamber or the cathode chamber in one of the unit cells, or the anode chamber or the cathode chamber in another of the unit cells adjacent to the one of the unit cells, and is equipped with an inlet for the oxygen-containing gas.

[10] The electrolytic cell according to [9], wherein the unit cells are connected with each other in the electrolytic cell, and the unit cells are arranged such that the sequence of the anode chamber, the cathode chamber, and the humidifying chamber is repeated.

EFFECTS OF THE INVENTION

[0009] According to the present invention, since the humidifying chamber is adjoined to and in heat exchange relation with the anode chamber or the cathode chamber, the oxygen-containing gas can be humidified with heat from the anode chamber or the cathode chamber, and overheating of the electrolytic cell can be suppressed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010]

FIG. 1 is a schematic cross-section view of an example of one of unit cells.
FIGs. 2(a) and 2(b) are schematic cross-section views of examples of the shape of an opening for supplying humidified oxygen-containing gas.
FIG. 3 is a schematic cross-section view of an example of one of unit cells equipped with a connecting pipe supplying humidified oxygen-containing gas.
FIG. 4 is a schematic cross-section view of an example of a monopolar electrolytic cell.
FIG. 5 is a schematic cross-section view of an example of a bipolar electrolytic cell.

MODE FOR CARRYING OUT THE INVENTION

[0011] Hereinafter, a two-chamber type electrolytic cell for saltwater and a method for producing sodium hydroxide and/or chlorine using the electrolytic cell according to the present invention will be described with reference to the drawings. The present invention, however, is not limited by the following drawings and can be altered in design within a scope in compliance with the intent described above and below.

[0012] FIG. 1 shows an example of one of unit cells in an electrolytic cell of the present invention. Unit cell 1 has an anode chamber 3, a cathode chamber 4, and an ion exchange membrane 2 sandwiched by the anode chamber 3 and the cathode chamber 4. The anode chamber 3 includes an anode 3a closely adjoining the anode side of the ion exchange membrane 2. The anode chamber 3 is also equipped with an inlet 3b for saltwater as a starting material at a lower part and equipped with an outlet 3c for electrolyzed saltwater and chlorine at an upper part. The cathode chamber 4 is equipped with a liquid retention layer 4b adjoining the cathode side of the ion exchange membrane 2, a gas-diffusion cathode 4a, and if necessary, a gas-diffusion cathode support 4c and a cushion material 4d in this order.

[0013] The unit cell 1 of the present invention is equipped with a humidifying chamber 5 separated from the cathode chamber 4 by a partition 6, and the humidifying chamber 5 is in heat exchange relation with the cathode chamber 4. The partition 6 exemplified in the drawing has a planar shape as shown in FIG. 2(a), and the space above the partition 6 in whole performs as an opening 7, which enable humidified oxygen-containing gas to be supplied from the humidifying chamber 5 to the cathode chamber 4. In addition, the cathode chamber 4 is also equipped with a pressure equalizing line 4e to keep water level in the humidifying chamber 5 constant. However, in the present invention, if another measure can keep the water level in the humidifying chamber 5 constant, the pressure equalizing line 4e is not required.

[0014] Water in the humidifying chamber may be in communication with the outside, or may not be in communication with the outside. In cases where the water is in communication with the outside, a line can be further provided to introduce water from the outside to the humidifying chamber and to discharge heated water to the outside (not shown in the figures). In the case where the water is introduced from the outside, the flow rate and the temperature of the water can be accordingly determined such that the water temperature in the humidifying chamber satisfies the predetermined condition (for example, 80°C or higher). However, in either case, whether the water is introduced or not introduced from the outside, it is preferable that the only heat produced by electrolytic reaction is used to heat the water up to the predetermined temperature in view of energy efficiency.

[0015] In the above unit cell 1, saltwater as a starting material is supplied from the inlet 3b for saltwater to the anode chamber 3, and at the same time, oxygen-containing gas is bubbled from an inlet 5a for oxygen-containing gas into water stored in the humidifying chamber 5 to generate the humidified oxygen-containing gas (oxygen concentration may be, for example, 90 % or more, preferably 93 % or more). By supplying the humidified oxygen-containing gas to the cathode chamber 4 and applying an electrical current, chlorine is generated at the anode 3a and sodium hydroxide is generated at the gas-diffusion cathode 4a. With progression of the electrolytic reaction of saltwater, heat generated at the cathode is conducted to the humidifying chamber 5, which can heat the water stored in the humidifying chamber 5 and facilitate vaporization of the water in the humidifying chamber. The following supply of the oxygen-containing gas to the humidifying chamber by means like bubbling can generate oxygen-containing gas including water vapor with an amount approximately equal to the saturation amount at the water temperature in the humidifying chamber. Therefore, without using extra energy other than the energy for electrolytic reaction, the efficiency of humidifying the oxygen-containing gas can be improved. Moreover, in the case where oxygen-containing gas that contains highly concentrated water vapor is supplied from a humidifier located outside the electrolytic cell, which is disclosed in the Patent Document 1, enough amount of water vapor cannot be supplied because of water condensation in a pipe during being supplied. Additionally, especially in an electrolytic cell having some unit cells, each of the unit cells may be supplied with a different amount of water because the degree of water condensation may vary in each of the unit cells. On the contrary, in the present invention, since each of the unit cells is equipped with the humidifying chamber, enough amount of water can be supplied to each of the unit cells without variation of the water amount. Furthermore, by conducting heat of the cathode chamber to the humidifying chamber, overheating of the unit cells, that is, overheating of the electrolytic cell, can be prevented without extra energy for cooling.

[0016] In the example of FIG. 1 described above, the humidifying chamber 5 is adjoined to the cathode chamber 4 in the unit cell 1. However, the humidifying chamber 5 may be adjoined to the anode chamber 3 (as described, the unit

cell equipped with the chambers in the sequence of the humidifying chamber 5, the anode chamber 3, and the cathode chamber 4 is hereinafter referred to as a B-type unit cell; the unit cell equipped with the chambers in the sequence of the anode chamber 3, the cathode chamber 4, and the humidifying chamber 5 is hereinafter referred to as a A-type unit cell.). Even in the case of the B-type unit cell, since the electrolytic reaction at the anode chamber 3 is an exothermal reaction, heat generated by the exothermal reaction can be used to heat the humidifying chamber 5 to improve the efficiency of generating water vapor. In addition, as described later, more than one B-type unit cells can be placed next to each other, and in such a case, the humidifying chamber 5 may be adjoined to the cathode chamber 4 of the adjacent unit cell. In this case, the exothermal reaction in the cathode chamber 4 in the adjacent unit cell can improve the efficiency of generating water vapor in the humidifying chamber 5.

[0017] Chlorine generated in the anode chamber 3 is discharged from the outlet 3c along with saltwater after electrolyzation. Sodium hydroxide generated in the cathode chamber 4 is transformed into aqueous sodium hydroxide having a concentration of about 32.0 % to 34.0 % with electro-osmotic water from the anode chamber 3 or moisture in the oxygen-containing gas transferred to the cathode chamber, which runs down the cathode chamber under its weight and is discharged along with exhaust gas of the oxygen-containing gas from an outlet 4g for electrolytic reactant. As described above, since enough amount of water can be supplied to the cathode in the present invention, the concentration of the aqueous sodium hydroxide can be kept from being too high, and as a result, damage of the gas-diffusion cathode 4a and the ion exchange membrane 2 can be prevented.

[0018] The partition 6 in the unit cell 1 may have at least one opening 7 having various shapes, as long as the partition 6 allows the humidified oxygen-containing gas to be communicated from the humidifying chamber 5 to the cathode chamber 4 through an upper side of the partition 6. For example, as shown in FIG. 2(b), the partition 6 may have a plurality of openings 7 on its upper side. The at least one opening 7 located at the upper side of the partition 6 may occupy the entire upper side of the partition 6 as shown in FIG. 2(a), or may occupy a part of the upper side of the partition 6 as shown in FIG. 2(b). Furthermore, the number of the at least one opening 7 is not particularly limited and may be one or more. Further, the shape of the at least one opening 7 is not particularly limited.

[0019] Moreover, the partition 6 may not have the at least one opening 7, as long as the humidified oxygen-containing gas is allowed to be communicated from the humidifying chamber 5 to the cathode chamber 4. For example, the humidified oxygen-containing gas may be supplied to the cathode chamber 4 through an external flow path such as a connecting pipe 8 as shown in FIG. 3. The unit cell 1 in FIG. 3 is the same as the unit cell in FIG. 1 except that the unit cell 1 in FIG. 3 is equipped with the connecting pipe 8 instead of the opening 7 shown in FIG. 1.

[0020] In the case where the aforementioned B-type unit cell is used, connecting the humidifying chamber 5 and the cathode chamber 4 by the connecting pipe 8 as described above enables the humidified oxygen-containing gas to be supplied from the humidifying chamber 5 to the cathode chamber 4. In addition, in the case where more than one B-type cell is placed next to each other, to enable the oxygen-containing gas to be supplied from the humidifying chamber 5 to the cathode chamber 4 of the adjacent unit cell, the opening 7 may be formed at the boundary of the humidifying chamber 5 and the cathode chamber 4 of the adjacent unit cell, or the connecting pipe 8 may be connected to the humidifying chamber 5 and the cathode chamber 4 of the adjacent unit cell.

[0021] In the unit cell as described above (including both the A-type unit cell and the B-type unit cell; the same applies hereafter), the anode 3a is not particularly limited, as long as it is an insoluble anode used for electrolysis of saltwater. For example, the anode may be such that coating of metal oxide including ruthenium oxide, titanium oxide, iridium oxide, or platinum-group metal oxides is applied on a base substance having a mesh structure such as expanded metal or fine mesh composed of metal including titanium.

[0022] The ion exchange membrane 2 is not particularly limited as long as it can be used for electrolysis of saltwater, and for example, it can be exemplified by a cation exchange membrane of perfluorocarbon-type, in which the ion exchange group is carboxyl acid and/or sulfonic acid.

[0023] The gas-diffusion cathode 4a is not particularly limited as long as it can be used for electrolysis of saltwater by the oxygen cathode method, and it is exemplified by a sheet-like triple-layer electrode in which a base material such as metal mesh-like material, carbon cloth, and/or hydrophobic resin is used, a reactive layer supported by a hydrophile catalyst is jointed on one side of the base material, and a water-shedding gas-diffusion layer is jointed on the other side of the base material. The catalyst can be exemplified by silver, platinum, gold, metal oxides, and carbon. The gas-diffusion cathode may be permeable to liquid, or may not permeable to liquid.

[0024] In the cathode chamber 4, absence of liquid between the ion exchange membrane 2 and the gas-diffusion cathode 4a makes it impossible for current to flow therebetween. While liquid can be retained between the ion exchange membrane 2 and the gas-diffusion cathode 4 by capillary action if the ion exchange membrane 2 and the gas-diffusion cathode 4 are closely attached to each other, it is preferable that the liquid retention layer 4b is placed between the ion exchange membrane 2 and the gas-diffusion cathode 4a to retain liquid more certainly. The liquid retention layer 4b enables liquid such as aqueous sodium hydroxide to be uniformly retained between the ion exchange membrane 2 and the gas-diffusion cathode 4a to prevent an increase in current density and voltage. Hydrophilicity and corrosion resistance are required for the liquid retention layer because the liquid retention layer needs to retain aqueous sodium hydroxide

(having a concentration of about 30 % and temperature of about 80°C to 90°C) generated by electrolytic reaction. Therefore, carbon materials such as carbon fibers and a porous structure composed of resin are preferably used.

[0025] An advantage of the two-chamber type method is that voltage can be made small due to small electric resistance between the electrodes since the anode, the ion exchange membrane, and the cathode are adjoined to each other. To closely attach the gas-diffusion cathode 4a to the ion exchange membrane 2 (if necessary, through the liquid retention layer 4b), it is preferable that the cushion material 4d is placed in a compressed state to generate reactive force, which is utilized to closely attach the gas-diffusion cathode 4a to the ion exchange membrane 2. In the two-chamber type method, separated by the ion exchange membrane, liquid pressure exerted by saltwater is applied to the anode chamber, and gas pressure is applied to the cathode chamber. The reactive force of the cushion material 4d is designed in conformity with the difference between the liquid pressure and the gas pressure. Since the deeper the depth of the saltwater is, the larger the liquid pressure is, making the reactive force of the cushion material at the lower side larger than at the upper side of the cathode chamber enables pressure applied to the ion exchange membrane or the anode electrode to be uniform. As such a cushion material 4d, a coiled material or a waved mat material can be used. Since the coiled material has elasticity in the diametrical direction and generates the reactive force in the diametrical direction, the coil axis can be placed parallel to the back board of the cathode gas chamber, and the reactive force of the cushion material can be designed to be larger at the lower side than at the upper side by selecting the wire diameter of the coil, the diameter of the coil material, and the laying density of the coil. As to the waved mat material, waved demister mesh in which metal wires are stocking stitched can be used, and the reactive force of the cushion material can be designed to be larger at the lower side than at the upper side by selecting the diameter of the wires, the number of the wires, and the number of the lamination layers of the mat material.

[0026] The gas-diffusion cathode support 4c can be placed between the cushion material 4d and the gas-diffusion cathode 4a, if necessary. The gas-diffusion cathode support 4c receives the reactive force of the cushion material 4d to allow the force to be uniformed and transmits the uniformed force to the gas-diffusion cathode 4a and the liquid retention layer 4b, and farther, the ion exchange membrane 2. As the gas-diffusion cathode support 4c, mesh materials such as a woven metal wire can be used.

[0027] Since both the cushion material 4d and the gas-diffusion cathode support 4c are placed in the cathode chamber, which is in a high corrosive environment because of high temperatures and the existence of highly concentrated oxygen and highly concentrated sodium hydroxide, it is preferable that nickel or nickel alloy whose nickel content is 20 % by weight or more, and silver plating thereof is used.

[0028] As the material for the walls constituting the anode chamber 3, titanium or titanium alloy whose titanium content is 20 % by weight or more is preferably used. As the material for the walls constituting the cathode chamber 4 and the humidifying chamber 5, nickel or nickel alloy whose nickel content is 20 % by weight or more, and silver plating thereof is preferably used.

[0029] In the present invention, more than one of the aforementioned unit cells (the A-type unit cells or the B-type unit cells, preferably the A-type unit cells) may be placed next to each other to compose the electrolytic cell. In this case, each of the unit cells may be connected in parallel electrically to compose a monopolar electrolytic cell, or each of the unit cells may be connected in series electrically to compose a bipolar electrolytic cell, and the bipolar electrolytic cell is preferable. Hereinafter, the monopolar electrolytic cell and the bipolar electrolytic cell will be explained referring to an example in which more than one of the A-type unit cells having the aforementioned opening 7 for the means of communication of the oxygen-containing gas between the humidifying chamber 5 and the cathode chamber 4 are placed next to each other. The following example may be applied to another example in which the connecting pipe 8 is used or in which more than one of the B-type cells are placed next to each other.

[0030] FIG. 4 is a schematic cross-section view of an example of a monopolar electrolytic cell, in which three of the A-type unit cells having the opening 7 are placed next to each other. In the monopolar electrolytic cell 10 shown in FIG. 4, more than one of the A-type unit cells (three of the A-type unit cells in the example of the figure), in which the aforementioned anode chamber 3, the cathode chamber 4, and the humidifying chamber 5 are placed in this sequence, can be arranged such that the sequence in each of the unit cells may be alternately reversed, such as the regular sequence (the anode chamber 3, the cathode chamber 4, and the humidifying chamber 5 are placed in this sequence), the reverse sequence (the humidifying chamber 5, the cathode chamber 4, and the anode chamber 3 are placed in this sequence), the regular sequence, and the reverse sequence. The anode electrodes of each of the unit cells are connected to an external electric source in parallel electrically respectively, and the cathode electrodes of each of the unit cells are also connected to the external electric source in parallel electrically respectively. The reference sign 9 shows a water storage tank for adjusting water level in the humidifying chamber. This example also allows heat of the cathode chamber 4 to be transmitted to the humidifying chamber 5 to humidify the oxygen-containing gas efficiently. In such an aforementioned example, in which more than one of the unit cells are placed next to each other such that the sequence in each of the unit cells may be alternately reversed, the humidifying chamber 5 of one of the unit cell (1) may be adjoined to the humidifying chamber 5 of the next unit cell (2). In this case, one humidifying chamber 5 may be shared by both the unit cell (1) and the unit cell (2).

[0031] FIG. 5 is a schematic cross-section view of an example of a bipolar electrolytic cell, in which four of the A-type unit cells having the opening 7 are placed next to each other. In the bipolar electrolytic cell 20 shown in FIG. 5, more than one of the unit cells 1 (four of the unit cells 1 in the example of the figure), each of which has the anode chamber 3 and the cathode chamber 4 internally having the humidifying chamber 5, are arranged such that the sequence of the anode chamber 3, the cathode chamber 4, and the humidifying chamber 5 is repeated. In the bipolar electrolytic cell 20, the anode electrode 3a in one unit cell (1) is capable of being electrically conducted to the cathode electrode 4a in the next unit cell (2) (not shown in the figure), and the cathode electrode 4a at one end and the anode electrode 3a at the other end are connected to an external electric source respectively to connect each of the unit cells in series electrically. Each of the inlets 3b for saltwater of the unit cells, each of the outlets 3c for electrolyzed saltwater and chlorine of the unit cells, each of the inlets 5a for oxygen-containing gas of the unit cells, each of water inlets 5b of the unit cells, each of the outlets 4g for electrolytic reactant of the unit cells, and each of the pressure equalizing lines 4e of the unit cells are respectively connected to each other by pipes, and the water inlets 5b and the pressure equalizing lines 4e are connected to the water storage tank 9. The mechanism of the electrolytic reaction in each of the unit cells of the bipolar electrolytic cell 20 is the same as in the aforementioned unit cells. However, because of the arrangement of the unit cells, each of the humidifying chambers 5 is adjoined not only to the cathode chamber 4 in the same unit cell but also to the anode chamber 3 in the next unit cell. Therefore, the humidifying chamber 5 can use heat generated by electrolytic reaction in both the anode chamber 3 and the cathode chamber 4 for humidification, which results in the increase of the heat efficiency in humidification. In addition, since the heat generated in the anode chamber 3 is transferred to the humidifying chamber 5, the anode chamber 3 can be cooled at the same time.

[0032] Moreover, in the case where more than one of the B-type unit cells (having the sequence of the humidifying chamber, the anode chamber, and the cathode chamber) are arranged regularly without alternately reversing the sequence of each of the unit cells to compose a bipolar electrolytic cell such as the example shown in FIG. 5, the humidifying chamber 5 is sandwiched by the anode chamber 3 and the cathode chamber 4. In this case, the humidifying chamber 5 can also use heat generated in both the anode chamber 3 and the cathode chamber 4 during humidification.

[0033] The present application claims priority based on Japanese Patent Application No. 2017-068057 filed on March 30, 2017. All the contents described in Japanese Patent Application No. 2017-068057 filed on March 30, 2017 are incorporated herein by reference.

EXAMPLES

[0034] Hereinafter, the present invention is more specifically described with reference to examples. The present invention, however, is not limited by the following examples but can also be absolutely carried out with appropriate changes to the examples within a scope in compliance with the intent described above and later, and all the changes are to be encompassed within a technical scope of the present invention.

Example 1

[0035] Five of the unit cells shown in FIG. 1 (except not having a gas-diffusion cathode support) were arranged such that the sequence of an anode chamber, a cathode chamber, and a humidifying chamber was repeated in this sequence, and were connected to each other in series electrically to compose a bipolar two-chamber type electrolytic cell for saltwater. DSE manufactured by De Nora Permelec Ltd. (insoluble metal in which metal base substance is coated with platinum-group metal or oxides thereof as a main component) was used as an anode electrode; gas-liquid transmissive carbon-silver electrode (GDE2013) manufactured by De Nora Permelec Ltd. was used as an cathode electrode; 4403D manufactured by Asahi Kasei Chemicals Corporation was used as an ion exchange membrane; carbon fiber woven fabric, the thickness of which is 0.45 mm, was used as a liquid retention layer; and silver-plated nickel wire in spiral shape was used as a cushion material.

[0036] Saltwater having a concentration of 218 g/L and a temperature of 53.8°C was supplied to the anode chamber at the rate of 183 L/m^2/h. Water was stored in the humidifying chamber, to which 1.5 times the theoretical requisite moles of oxygen-containing gas (corresponds to "oxygen-containing gas supplied to electrolytic cell" shown in the below table 1) having a temperature of 25°C and a concentration of 93.0 % was supplied by bubbling. The temperature of the humidifying chamber was 84.0 °C, and therefore, at the time when being supplied to the cathode chamber, the temperature of the humidified oxygen-containing gas was about 84.0°C. The saltwater was electrolyzed at the current density of 5.65 kA/m^2, and each value was measured after ten days of the electrolyzation.

Comparative Example 1

[0037] Except not having the humidifying chamber in a unit cell, five of the same unit cells as Example 1 having the same material of the anode electrode, the cathode electrode, the ion exchange membrane, etc. and the same size of

the cathode chamber, the anode chamber, etc. were arranged such that the sequence of the anode chamber, and the cathode chamber is repeated in this sequence, and were connected to each other in series electrically to compose a conventional bipolar two-chamber type electrolytic cell for saltwater (not shown in the figures).

[0038] Saltwater having a concentration of 219 g/L and a temperature of 51.4°C was supplied to the anode chamber at the rate of 183 L/m^2/h. The cathode chamber of each of the unit cells was connected to a humidifier prepared outside the electrolytic cell. In the humidifier, 1.5 times the theoretical requisite moles of oxygen-containing gas having a concentration of 93.0 % was bubbled into the water (25°C) in the humidifier to generate humidified oxygen-containing gas having a temperature of 25°C, which was supplied to the cathode chamber at the same temperature. The saltwater was electrolyzed at the current density of 5.65 kA/m^2, and each value was measured after ten days of the electrolyzation. Being different from Example 1, Comparative Example 1 did not have the humidifying chamber in the unit cell and the humidified oxygen-containing gas was supplied from the external humidifier, and therefore, the meaning of "oxygen-containing gas supplied to electrolytic cell" and "oxygen-containing gas supplied to cathode chamber" shown in the below table 1 are identical in meaning (the same applies to the following Comparative Examples 2 to 4).

Comparative Example 2

[0039] In the same manner as in Comparative Example 1 except that the water temperature of the external humidifier in Comparative Example 1 was altered to 84°C, and that humidified oxygen-containing gas generated at 84°C was supplied to the cathode chamber at the same temperature (heat input rate to the humidifier was about 5.2 MJ/m^2/h), each value was measured after ten days of the electrolyzation.

Comparative Example 3

[0040] With the same composition as in Comparative Example 2, additionally, heat-retention around the pipe connecting the humidifier and the anode chamber of each of the unit cells was improved to prevent the temperature of the humidified oxygen-containing gas from decreasing, and each value was measured after ten days of the electrolyzation. The heat input rate to the humidifier was about 5.2 MJ/m^2/h, which was the same as in Comparative Example 2.

Example 2

[0041] The same electrolytic cell as in Example 1 was operated for 300 days, after which each value was measured.

Comparative Example 4

[0042] The same electrolytic cell as in Comparative Example 1 was operated for 300 days, after which each value was measured.

[0043] The measurement results of the Examples and the Comparative Examples are shown in Table 1 and Table 2. Table 2 shows both the average value of five of the unit cells and the difference between the average value and each value of five of the unit cells in the concentration of generated sodium hydroxide and current efficiency.

[Table 1]

	Current density (kA/m^2)	Supplied Saline water			Liquid in anode compartment		Oxygen-containing gas supplied to electrolysis cell			Oxygen-containing gas supplied to cathode compartment	Cell voltage (V)	Temperature in humidifying compartment (°C)	Temperature of catode (°C)	Temperature of exhaust gas (°C)	Average concentration of generated NaOH (%)	Current efficiency (%)
		Amount ($L/m^2/h$)	Concentration (g/L)	Temperature (°C)	Concentration (g/L)	Temperature (°C)	Concentration (%)	Multiple of theoretical amount	Temperature (°C)	Temperature (°C)						
Example 1	5.65	183	218	53.8	173	84.0	93.0	×1.5	25.0	84.0	2.30	84.0	82.0	82.0	32.2	96.5
Comparative Example 1	5.65	183	219	51.4	174	84.0	93.0	×1.5	25.0	25.0	2.32	-	75.0	75.0	34.6	96.5
Comparative Example 2	5.65	183	219	47.0	174	84.0	93.0	×1.5	84.0	84.0	2.30	-	82.0	82.0	32.2	96.4
Comparative Example 3	5.65	183	219	47.0	174	84.0	93.0	×1.5	84.0	84.0	2.30	-	82.0	82.0	32.2	96.5
Example 2	5.65	183	218	53.3	173	84.0	93.0	×1.5	25.0	84.0	2.35	84.0	82.0	82.0	32.2	96.3
Comparative Example 4	5.65	183	219	51.0	174	84.0	93.0	×1.5	25.0	25.0	2.43	-	75.0	75.0	34.6	96.0

[Table 2]

	Concentration of generated NaOH						Current efficiency					
	Average (%)	#1	#2	#3	#4	#5	Average (%)	#1	#2	#3	#4	#5
Example 1	32.2	-0.2%	+0.1%	+0.1%	+0.2%	-0.2%	96.5	-0.2%	+0.1%	0%	+0.2%	-0.1%
Comparative Example 1	34.6	-0.2%	+0.2%	+0.1%	+0.1%	-0.2%	96.5	-0.3%	+0.1%	+0.1%	0%	+0.1%
Comparative Example 2	32.2	+0.5%	-0.2%	-0.4%	-0.2%	+0.3%	96.4	-0.4%	+0.2%	+0.3%	+0.2%	-0.3%
Comparative Example 3	32.2	-0.1%	+0.2%	+0.2%	0%	-0.3%	96.5	-0.2%	+0.2%	+0.1%	0%	-0.1%
Example 2	32.2	-0.1%	+0.1%	0%	+0.2%	-0.2%	96.3	-0.2%	+0.1%	0%	+0.2%	-0.1%
Comparative Example 4	34.6	0%	+0.2%	+0.1%	-0.1%	-0.2%	96.0	-0.3%	+0%	+0.2%	+0.2%	-0.1%

[0044] In Example 1, due to the reaction heat, the temperature of the humidifying chamber was equivalent to the temperature of the anode chamber, and the concentration of generated sodium hydroxide was 32.2 %, not too high, which shows that enough amount of water vapor was supplied (Table 1). In addition, variation in the concentration of generated sodium hydroxide and in current efficiency in each of five unit cells could be made small, which shows that the variation in the amount of the water vapor supplied to the anode chamber of each of the unit cells was small (Table 2). Moreover, Example 2, in which the electrolyzation was operated longer than in Example 1, showed good current efficiency of 96.3 % even after 300 days, as well as good results in other values almost the same as in Example 1. Since enough amount of water vapor could be supplied in Example 2, low concentration of generated sodium hydroxide could be maintained, and since damage of the gas-diffusion cathode was prevented in Example 2, the difference in voltage of the gas-diffusion cathode after 300 days of electryzation was as small as 45 mV on average. The differences in voltage of the gas-diffusion cathode in each of the unit sells were 78 mV, 15 mV, 45 mV, 33 mV, and 54 mV respectively.

[0045] On the other hand, in Comparative Example 1, in which humidified oxygen-containing gas was supplied from the external humidifier, since the temperature of the external humidifier was 25.0°C, the pressure of water vapor in the gas was low, and the concentration of generated sodium hydroxide was as high as 34.6 %, which shows that the supplied amount of water vapor was insufficient (Table 1).

[0046] Comparative Example 2 was an example in which the temperature of the external humidifier was altered to 84°C to increase the water vapor pressure in the oxygen-containing gas, which required energy to raise water temperature in the external humidifier. The average concentration of generated sodium hydroxide was 32.2 %, which means that enough amount of water vapor could be supplied on the average, however, as shown in Table 2, the variation in both the concentration of sodium hydroxide and current efficiency of each unit cell became large. The reason of this is considered that water was condensed in the process where the oxygen-containing gas was supplied from the external humidifier to the cathode chamber of each of the unit cells, and the degree of the condensation was different in each of the unit cells. In addition, since the oxygen-containing gas of high temperature was supplied from outside the electrolytic cell, the saltwater supplied to the anode electrode was required to have a low temperature to prevent the electrolytic cell from overheating (while the temperature of the supplied saltwater in Example 1 was 53.8°C, which is within the usual range of the temperature in saltwater electrolysis plants, the temperature of the supplied saltwater in Comparative Example 2 was 47.0°C.), and thus, extra energy was required for cooling the supplied saltwater.

[0047] Comparative Example 3 was an example in which heat-retention of the pipe from the external humidifier in Comparative Example 2 was improved, and required extra energy for heating in the external humidifier, which is the same as in Comparative Example 2. In Comparative Example 3, water condensation was suppressed in the pipes, and as a result, the variations in the concentration of the generated sodium hydroxide and the current efficiency of each of the unit cells could be made small, however, extra energy for cooling the supplied saltwater was required in the same manner as in Comparative Example 2.

[0048] Comparative Example 4 was an example in which the electrolytic cell was operated for 300 days in the same condition as in Comparative Example 1, and the difference in the voltage of the gas-diffusion cathode after 300 days of electrolyzation was 108 mV on average of five of the unit cells, which was much higher than in Example 2, and current efficiency was 96.0 %, which was lower than in Example 2. The reason of this is considered that as the same as in Comparative Example 1, the concentration of generated sodium hydroxide was 34.6 % in Comparative Example 4, which was 2 % or higher than the concentration of sodium hydroxide of 32.2 % in Examples 1 and 2, and as a result, the gas-diffusion cathode was damaged. The differences in voltage of the gas-diffusion cathode in each of the unit sells were 123 mV, 66 mV, 114 mV, 108 mV, and 129 mV respectively.

DESCRIPTION OF REFERENCE SIGNS

[0049]

1: unit cell
2: ion exchange membrane
3: anode chamber
3a: anode electrode
4: cathode chamber
4a: gas-diffusion cathode
5: humidifying chamber
6: partition
7: opening
8: connecting pipe
10: monopolar electrolytic cell
20: bipolar electrolytic cell

Claims

1. A method for producing sodium hydroxide and/or chlorine by electrolyzing saltwater, the method comprising using a two-chamber type electrolytic cell for saltwater comprising one or more unit cells equipped with an anode chamber including an anode, a cathode chamber including a gas-diffusion cathode, and an ion exchange membrane sandwiched by the anode chamber and the cathode chamber,
supplying saltwater to the anode chamber, and
supplying humidified oxygen-containing gas to the cathode chamber, wherein
each of the unit cells further comprises a humidifying chamber generating the humidified oxygen-containing gas that is to be supplied to the cathode chamber,
the humidifying chamber is adjoined to and in heat exchange relation with the anode chamber or the cathode chamber in one of the unit cells, or is adjoined to and in heat exchange relation with the anode chamber or the cathode chamber in another of the unit cells adjacent to the one of the unit cells, and
the oxygen-containing gas is humidified by generating water vapor with heat from the anode chamber or the cathode chamber.

2. The method according to claim 1, wherein the humidifying chamber is adjoined to the cathode chamber, and the humidified oxygen-containing gas generated in the humidifying chamber is supplied from the humidifying chamber to the cathode chamber through at least one opening located at a partition between the humidifying chamber and the cathode chamber.

3. The method according to claim 2, wherein the at least one opening located at the partition between the humidifying chamber and the cathode chamber comprises a single opening.

4. The method according to claim 2, wherein the at least one opening located at the partition between the humidifying chamber and the cathode chamber comprises a plurality of openings.

5. The method according to claim 1, wherein the humidified oxygen-containing gas generated in the humidifying chamber is supplied from the humidifying chamber to the cathode chamber through at least one flow path located outside the humidifying chamber and the cathode chamber.

6. The method according to claim 5, wherein the at least one flow path located outside the humidifying chamber and the cathode chamber comprises a single flow path.

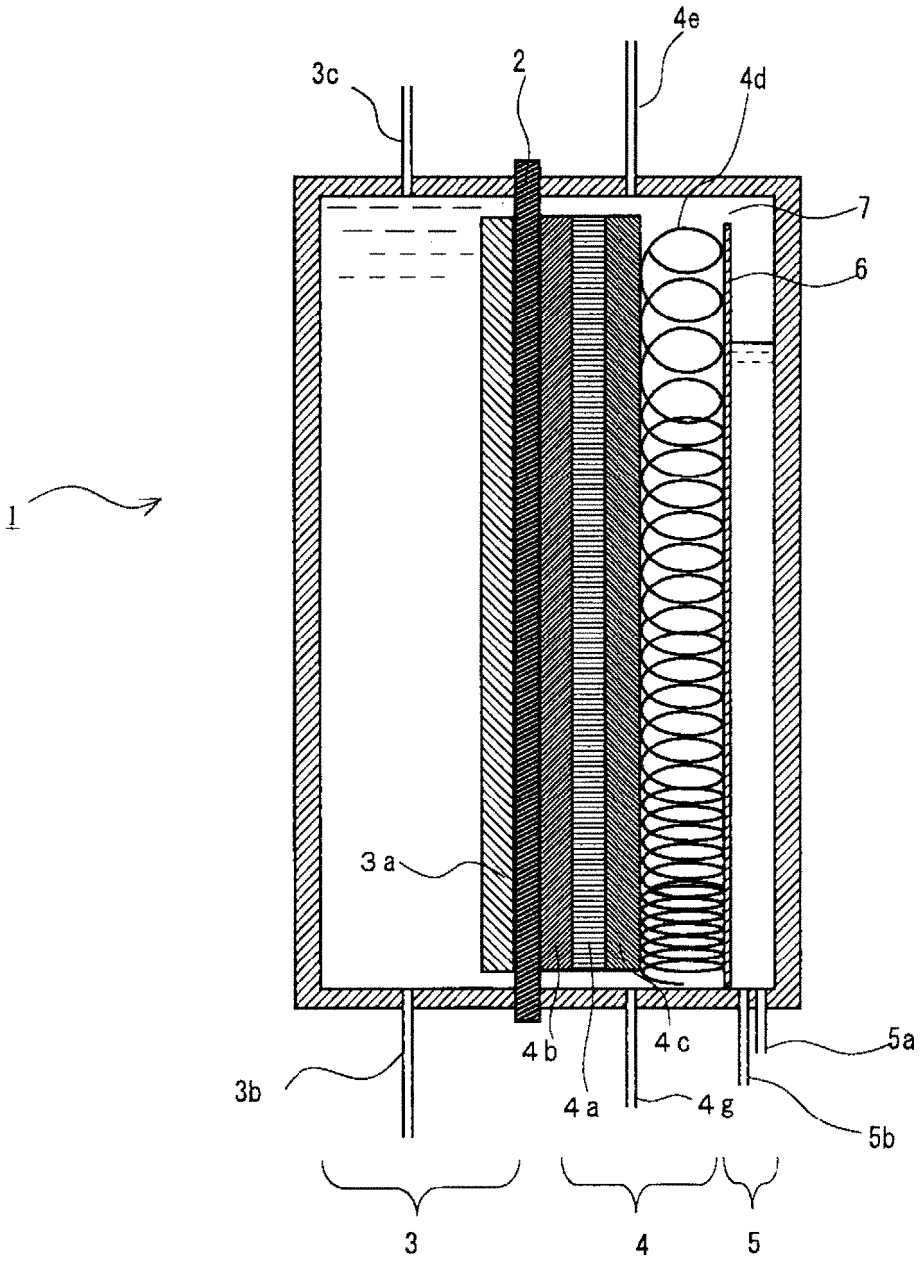
7. The method according to claim 5, wherein the at least one flow path located outside the humidifying chamber and the cathode chamber comprises a plurality of flow paths.

8. The method according to any one of claims 1 to 7, wherein the unit cells are connected with each other in the electrolytic cell, and the unit cells are arranged such that the sequence of the anode chamber, the cathode chamber, and the humidifying chamber is repeated.

9. A two-chamber type electrolytic cell for saltwater, comprising one or more unit cells equipped with an anode chamber, a cathode chamber, and an ion exchange membrane sandwiched by the anode chamber and the cathode chamber, wherein
the anode chamber includes an anode, and is equipped with an inlet for saltwater as a starting material, an outlet for electrolyzed saltwater, and an outlet for chlorine,
the cathode chamber includes a gas-diffusion cathode, and is equipped with an inlet for humidified oxygen-containing gas and an outlet for electrolytic reactant,
each of the unit cells further comprises a humidifying chamber generating oxygen-containing gas that is to be supplied to the cathode chamber, and
the humidifying chamber is adjoined to and in heat exchange relation with the anode chamber or the cathode chamber in one of the unit cells, or is adjoined to and in heat exchange relation with the anode chamber or the cathode chamber in another of the unit cells adjacent to the one of the unit cells, and is equipped with an inlet for the oxygen-containing gas.

10. The electrolytic cell according to claim 9, wherein the unit cells are connected with each other in the electrolytic cell, and the unit cells are arranged such that the sequence of the anode chamber, the cathode chamber, and the humidifying chamber is repeated.

FIG. 1



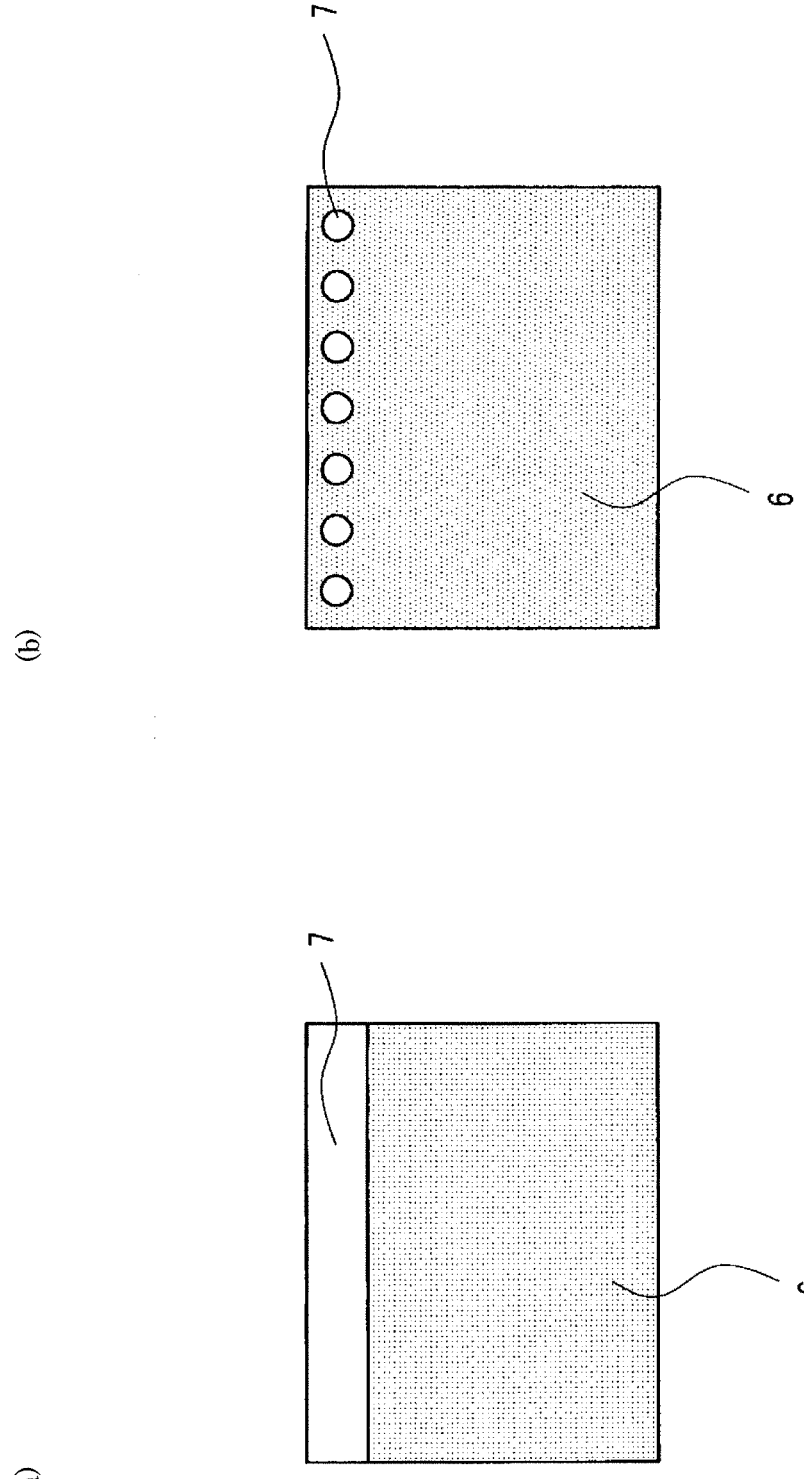


Fig. 2

FIG. 3

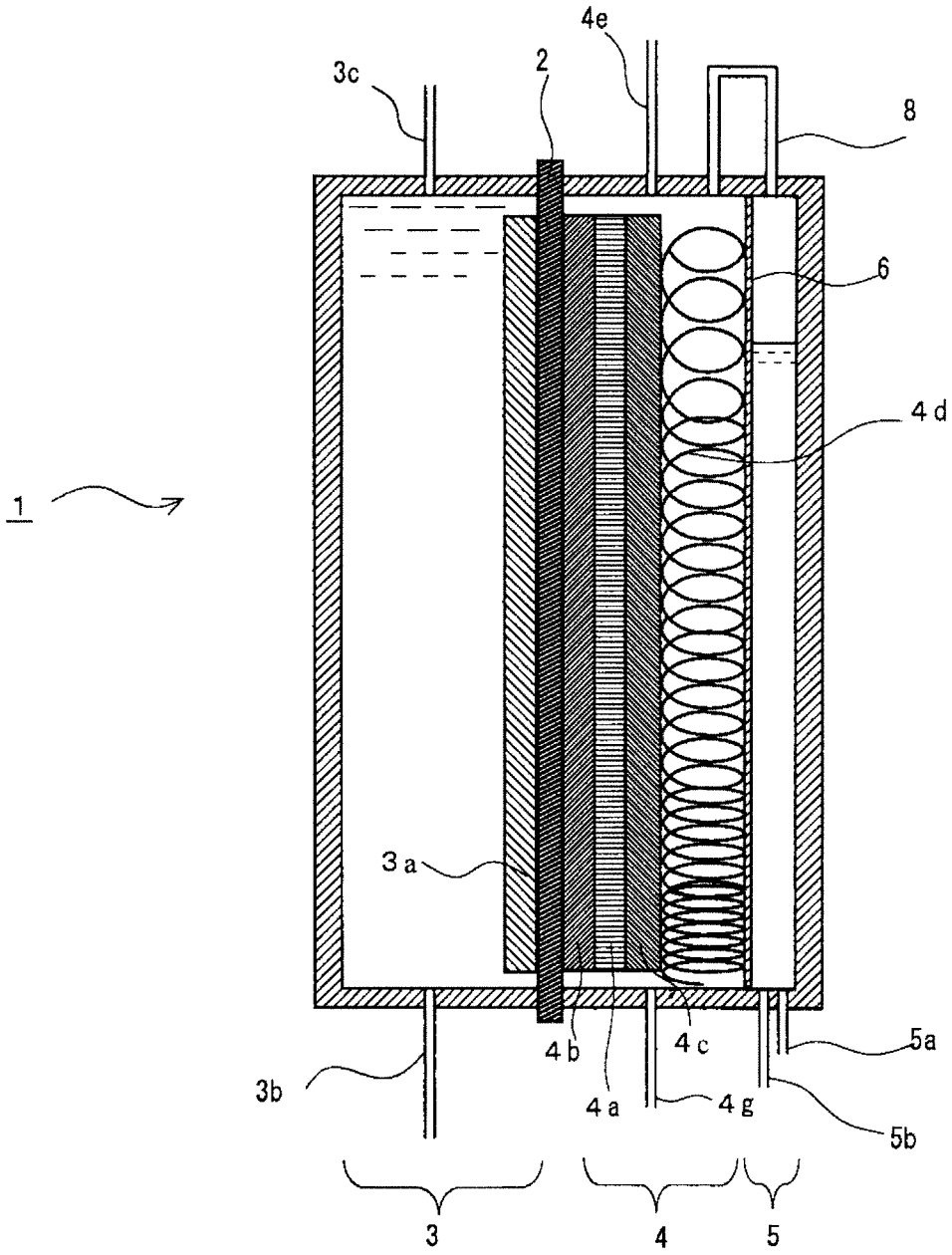
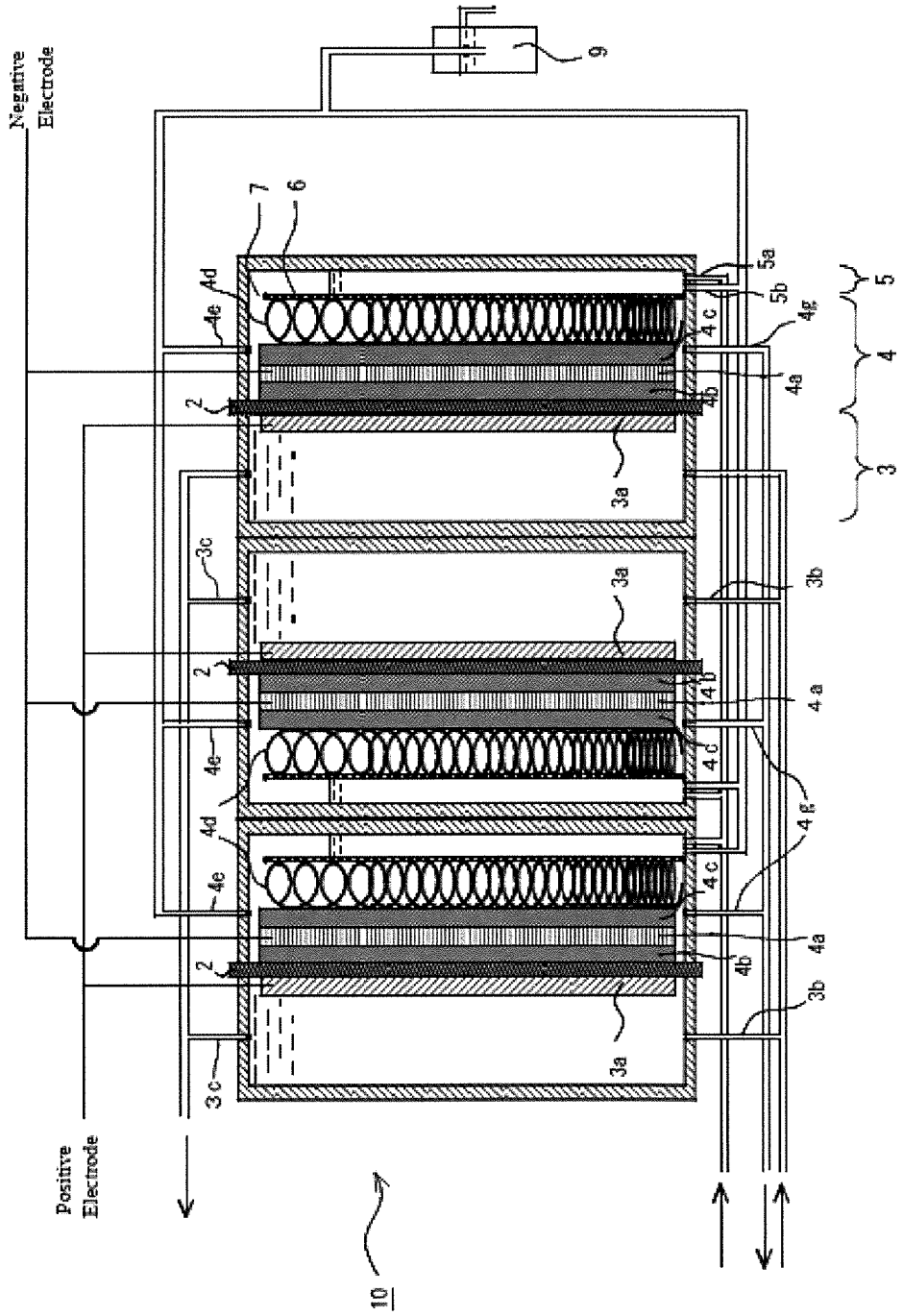


FIG.4


Negative Electrode
Positive Electrode
9
10
7
6
5a
5b
4g
4c
4a
4b
4d
4e
2
3a
3b
3c
5
4
3

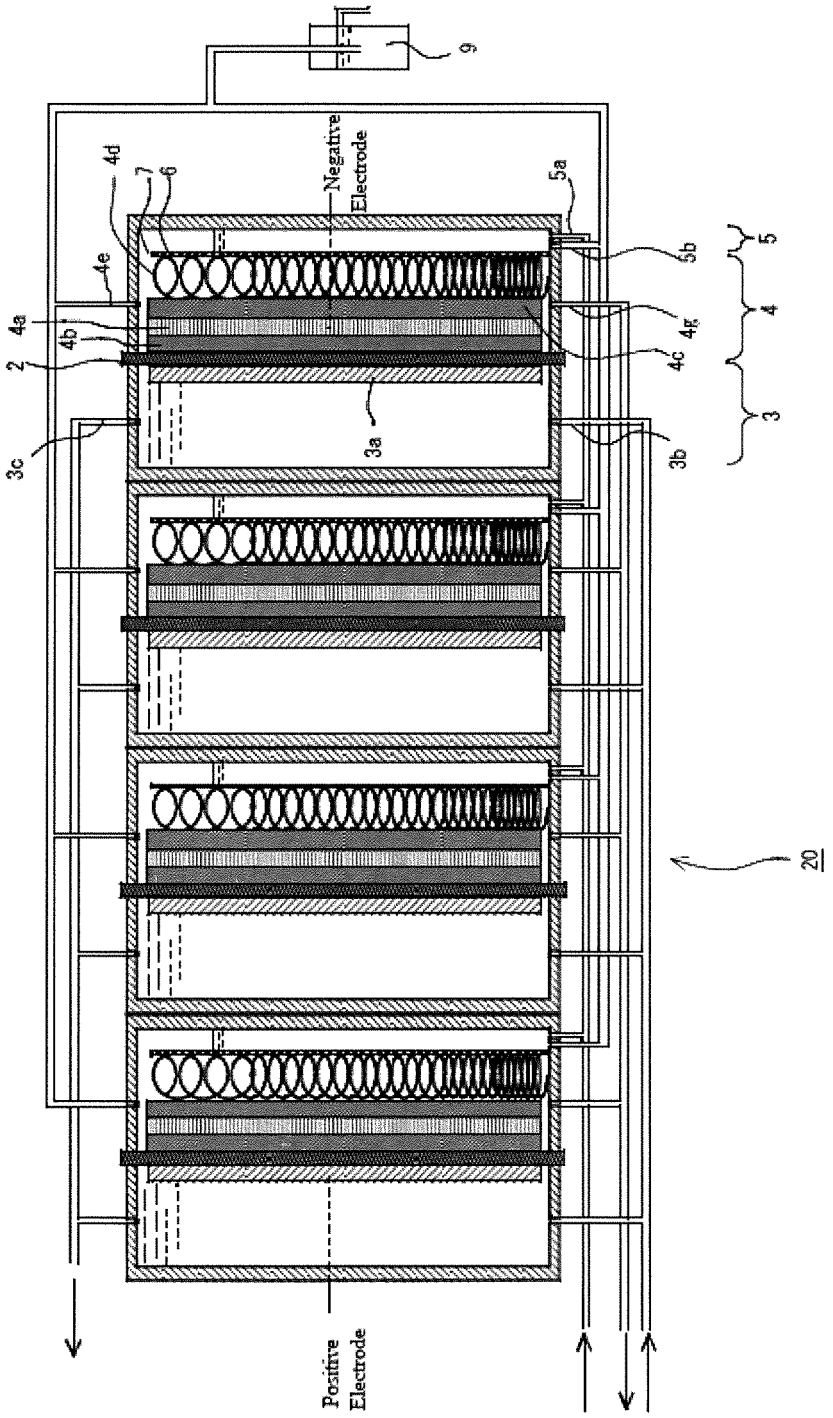

9
Negative Electrode
4d
7
6
5a
4e
5b
5
4
4a
4b
2
4c
3
3a
3c
3b
20
Positive Electrode

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/010870

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl. C25B1/34(2006.01)i, C25B9/00(2006.01)i, C25B9/10(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int. Cl. C25B1/34, C25B9/00, C25B9/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2018
Registered utility model specifications of Japan 1996-2018
Published registered utility model applications of Japan 1994-2018

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2003-041388 A (ASSOCIATION FOR THE PROGRESS OF NEW CHEMISTRY) 13 February 2003, entire text (Family: none)	1-10
A	JP 2010-275579 A (CHLORINE ENGINEERS LTD.) 09 December 2010, entire text (Family: none)	1-10
A	JP 2012-184507 A (BAYER MATERIALSCIENCE AG) 27 September 2012, entire text & US 2012/0222965 A1, entire text & EP 2495353 A2 & DE 102011005133 A1 & CN 102653871 A	1-10
A	WO 2016/148637 A1 (H2SG ENERGY PTE LTD.) 22 September 2016, entire text & US 2017/0152605 A1 & CN 106661741 A & CA 2979659 A1	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
23.05.2018	05.06.2018
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

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- JP 2017068057 A **[0033]**