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(54) **ELECTRODE UNIT, ELECTROLYTIC CELL COMPRISING ELECTRODE UNIT AND ELECTROLYTIC DEVICE**

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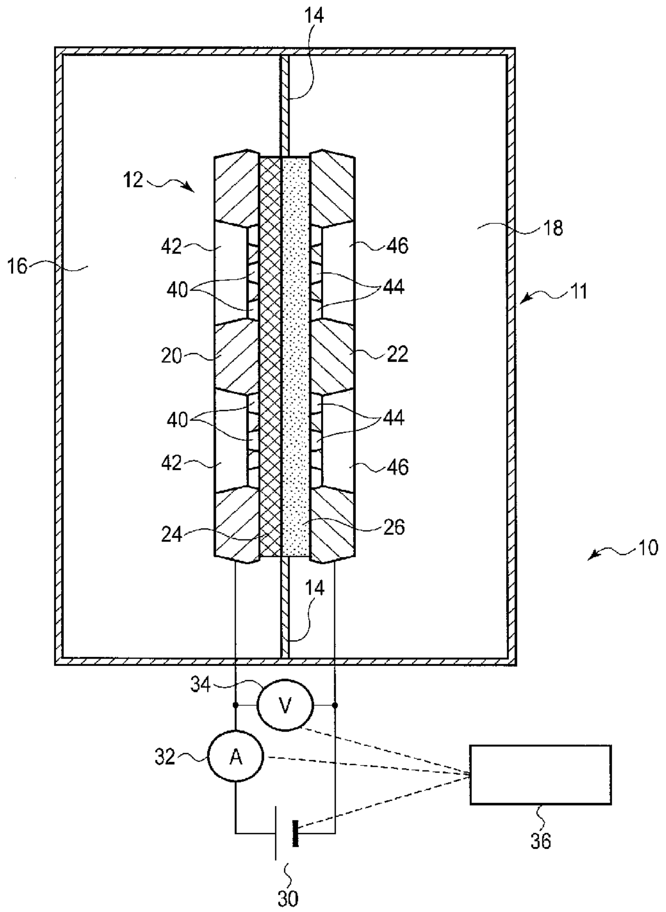
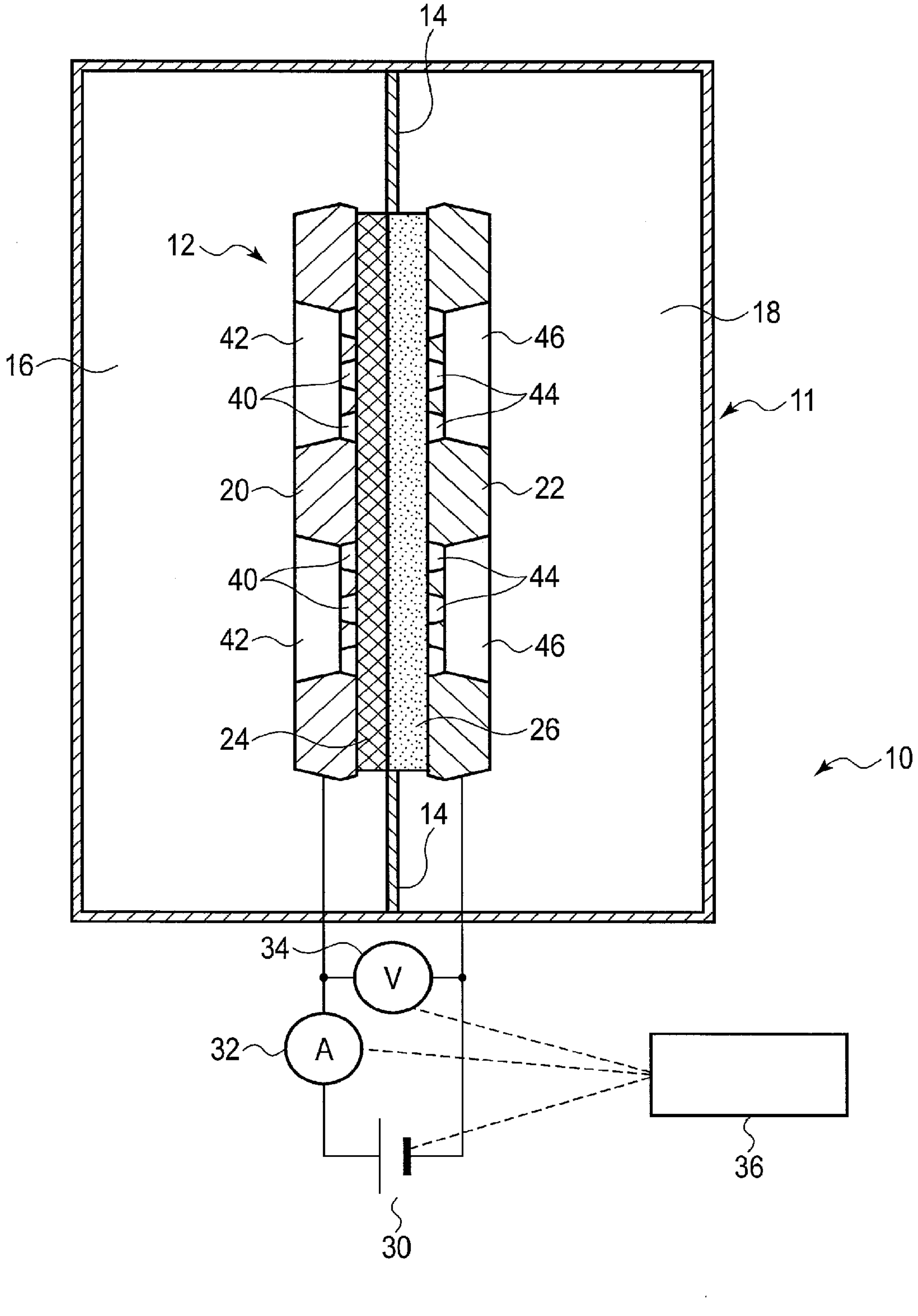
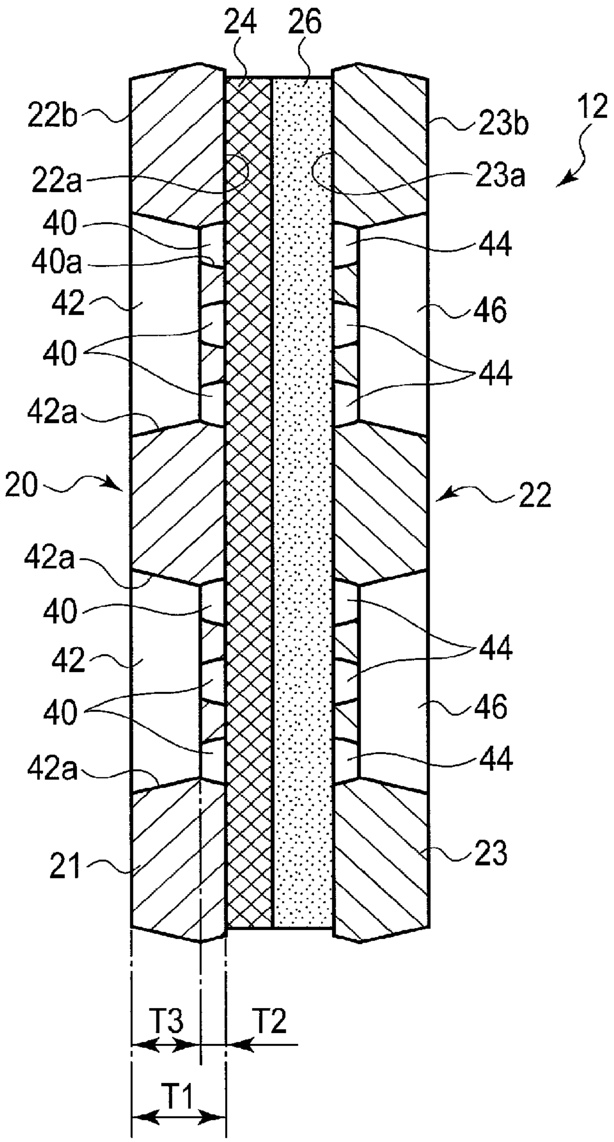
(57) **ABSTRACT**

According to one embodiment, an electrode unit of an electrolytic device includes a first electrode including a first surface, a second surface located on an opposite side to the first surface, a plurality of first pores opened in the first surface, a plurality of second pores opened in the second surface and having an opening area greater than that of the first pores, and a plurality of the first pores communicating with a respective one of the second pores, a second electrode opposing the first surface of the first electrode, and a continuous porous membrane arranged between the first electrode and the second electrode, so as to cover the first surface of the first electrode.





F I G. 1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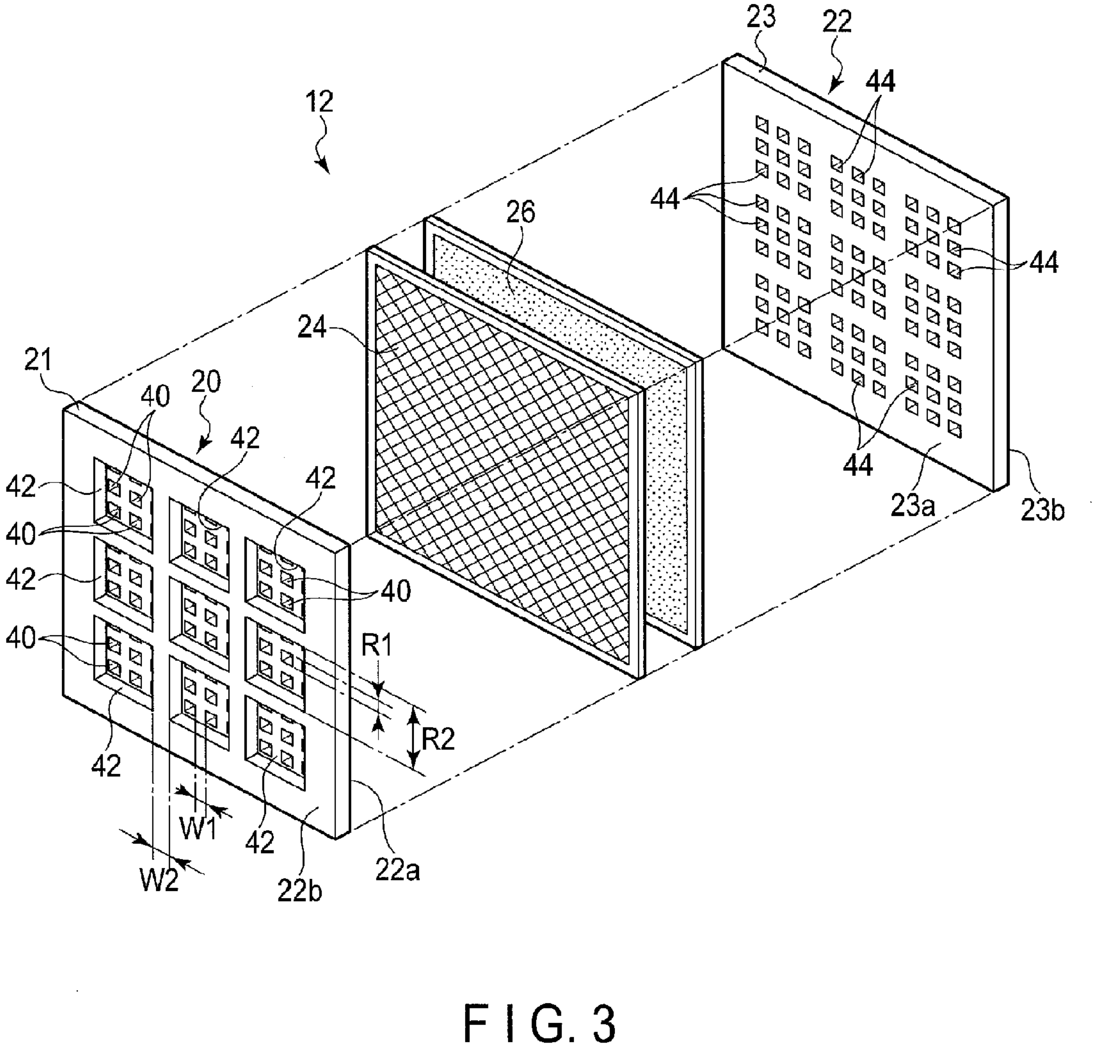
T3
T2
T1

F I G. 2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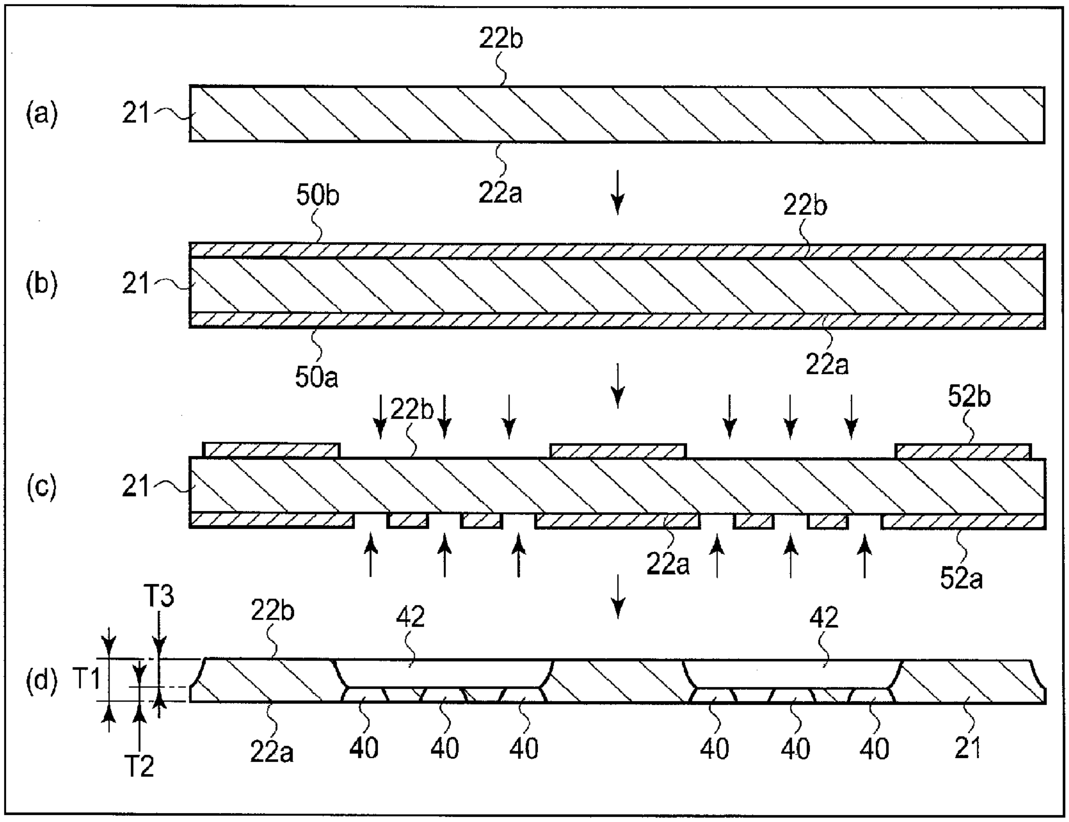
22a
23a
23b

FIG. 3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22b
22a
(b)
50b
22b
50a
22a
(c)
22b
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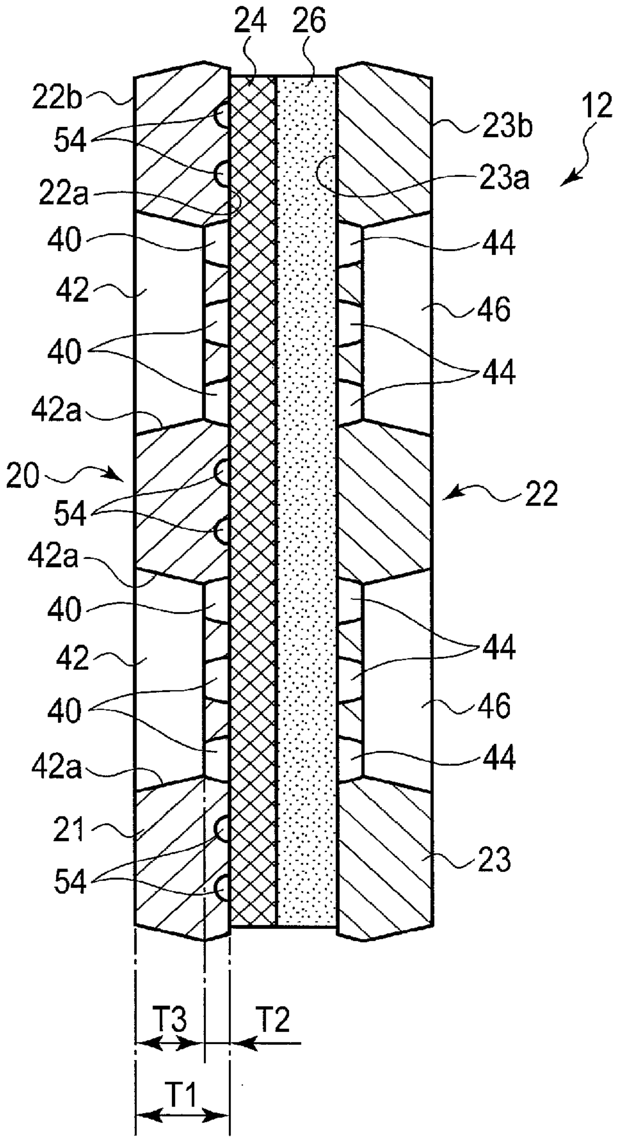
52a
(d)
T1
T2
T3
22b
22a
42
42
40
21

F I G. 4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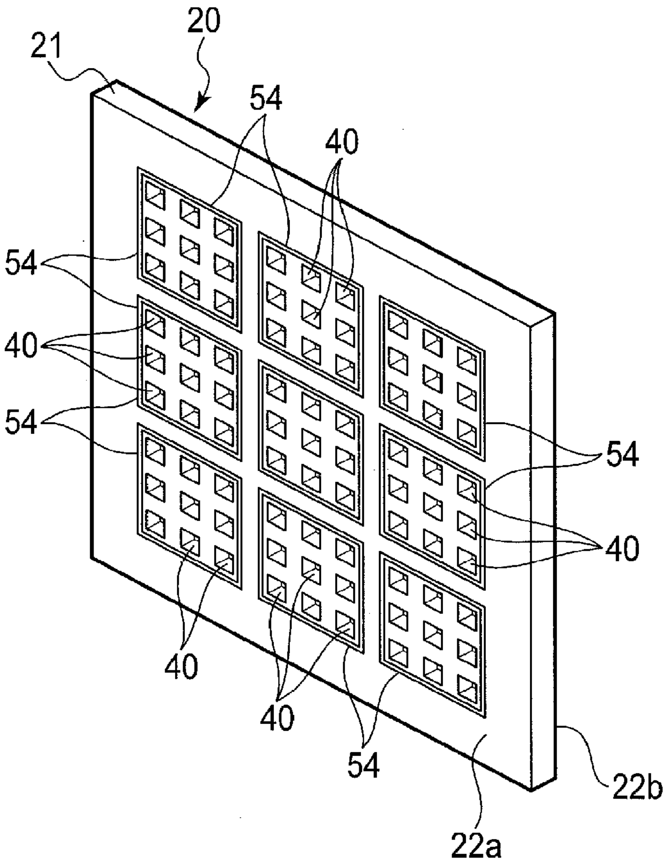
23
T3
T2
T1

FIG. 5



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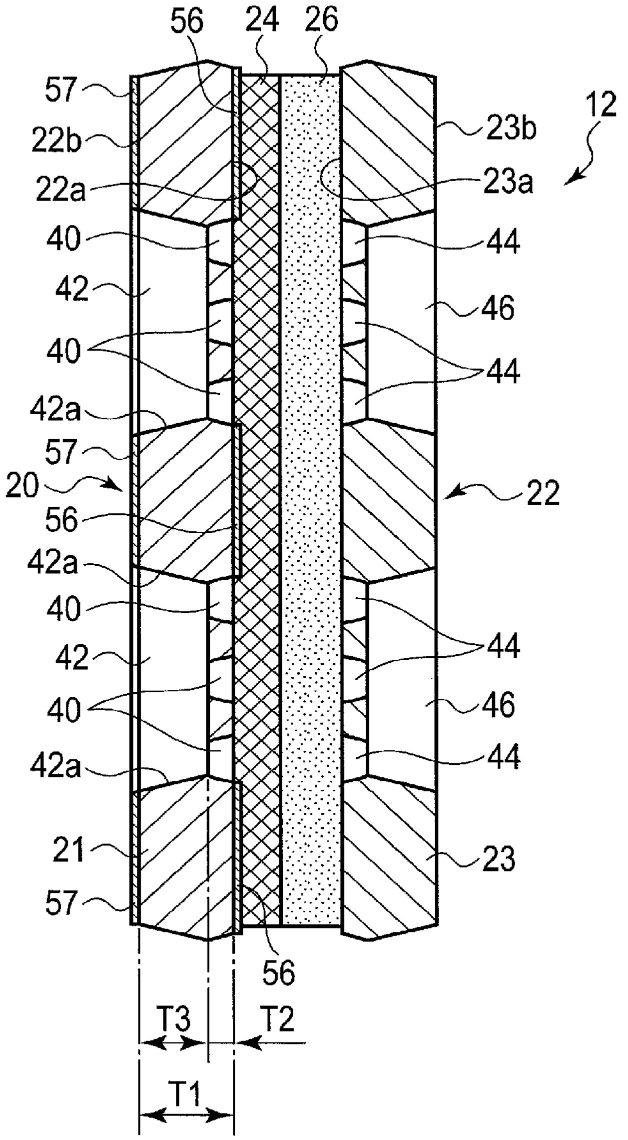
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42a
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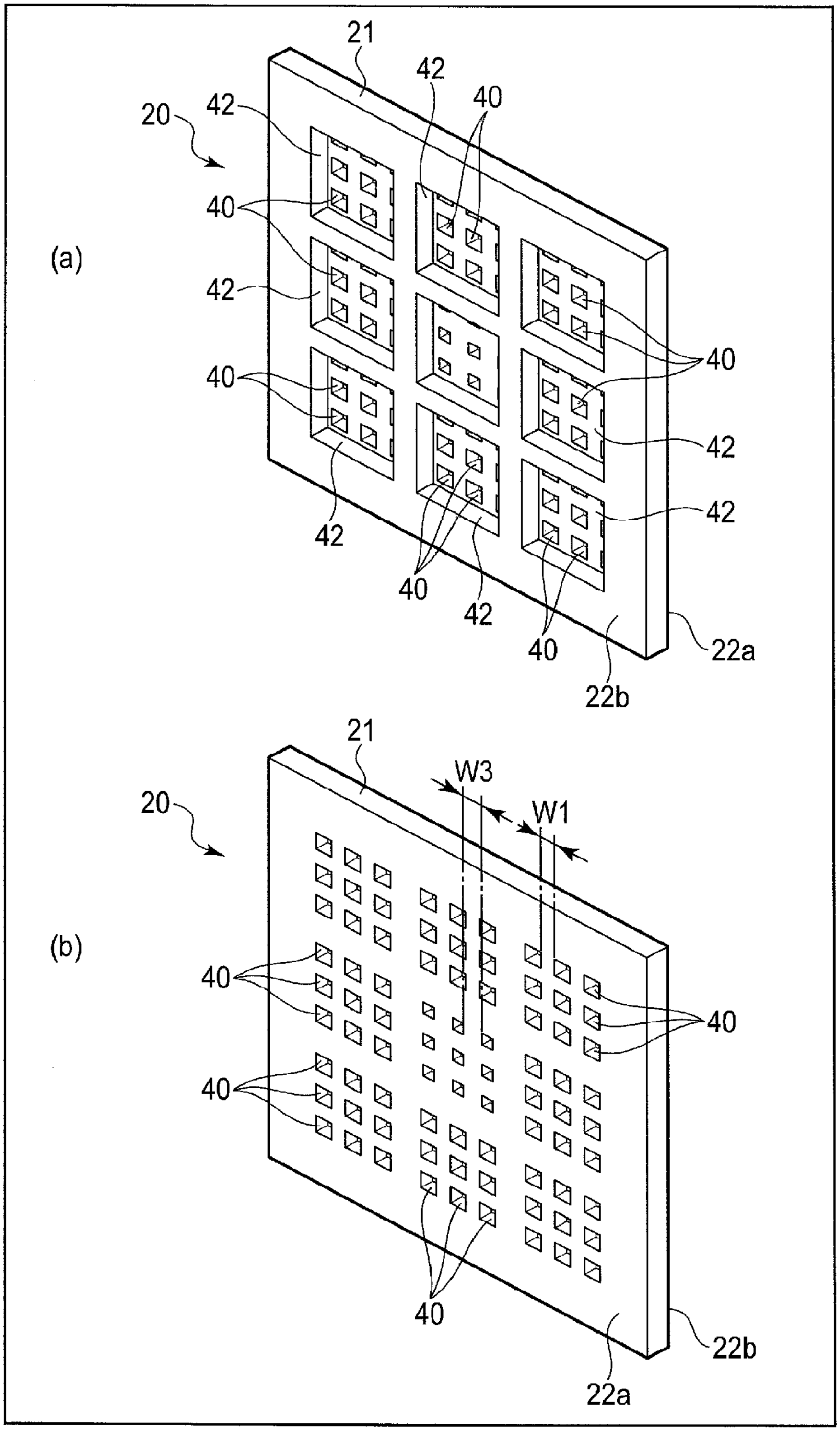
44
23
T3
T2
T1

FIG. 7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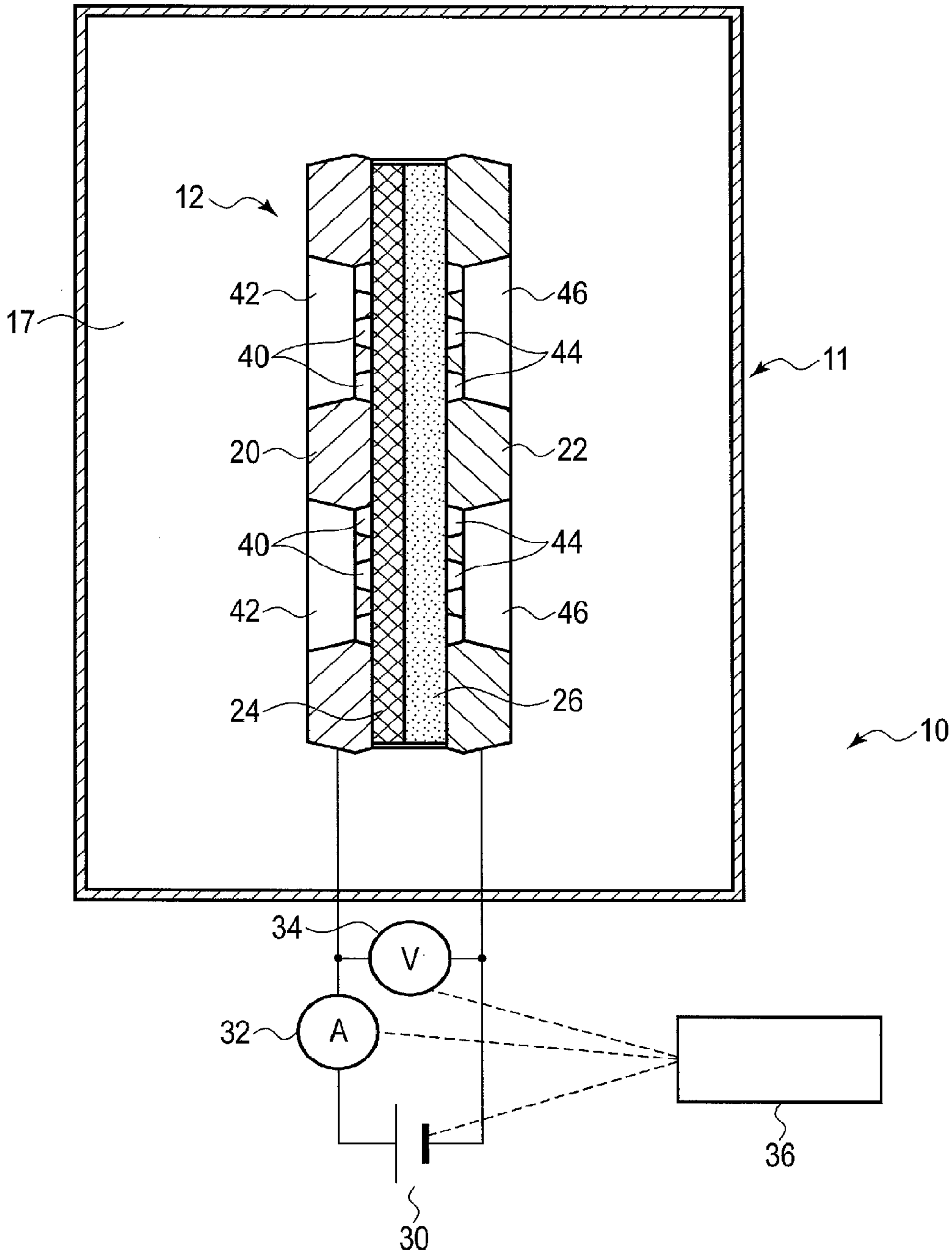
22b
22a

F I G. 8



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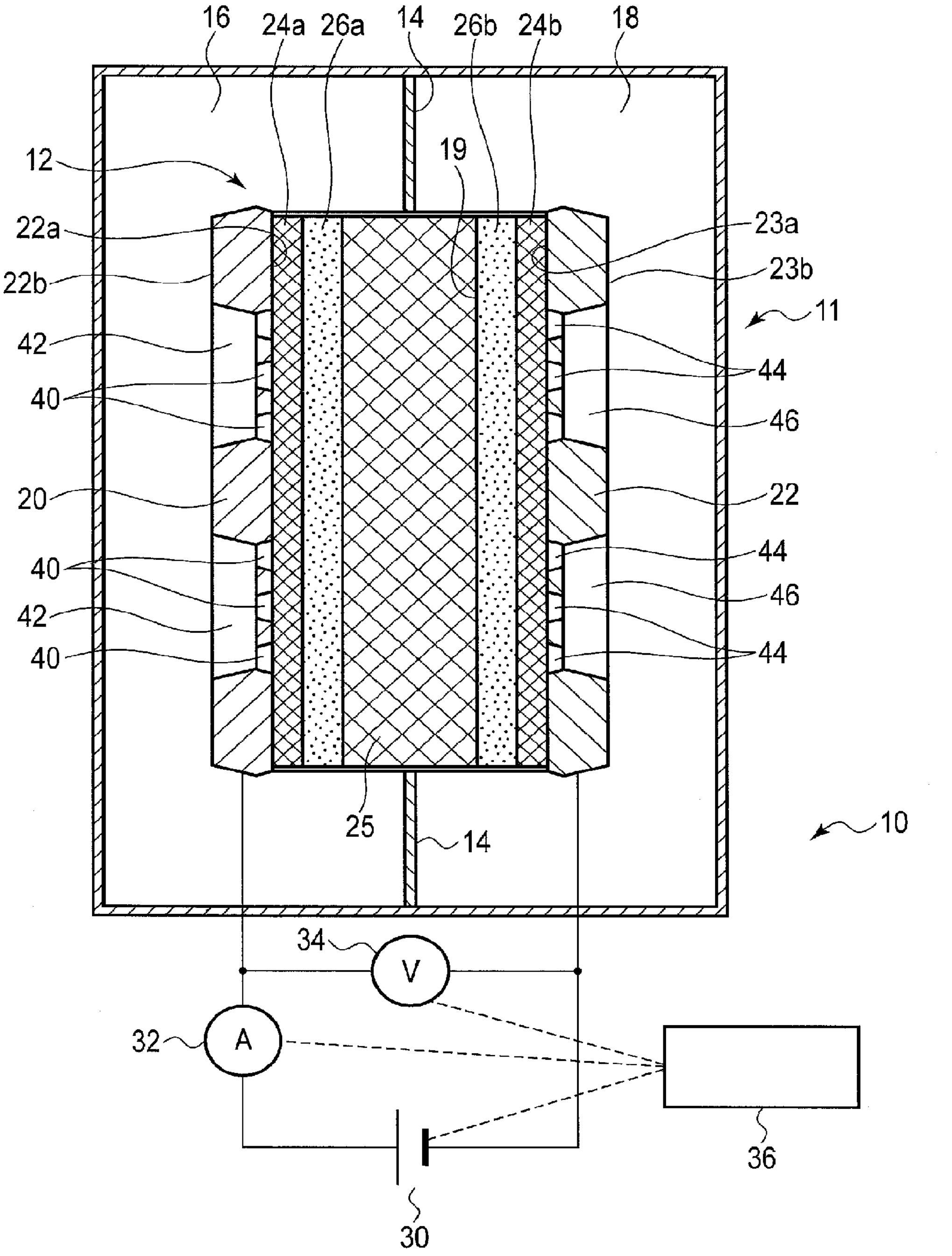
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22b
23b
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V
32
A
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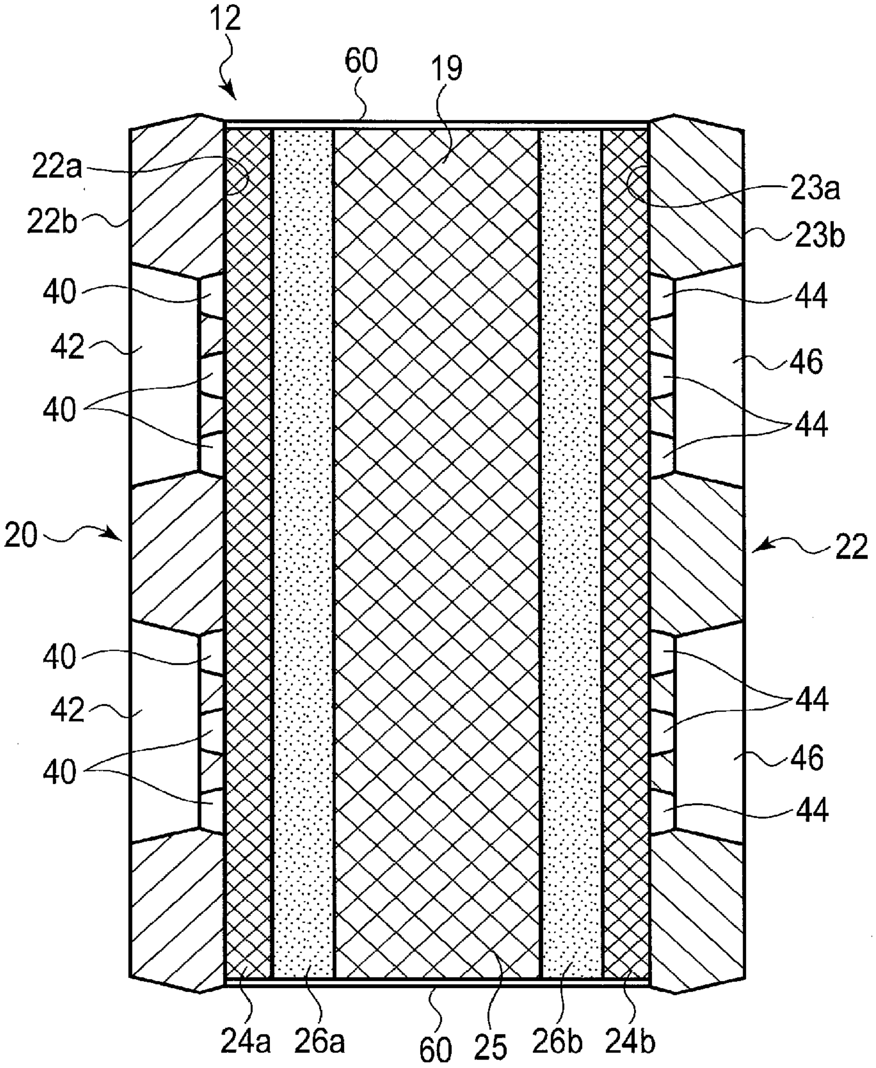
30

F I G. 10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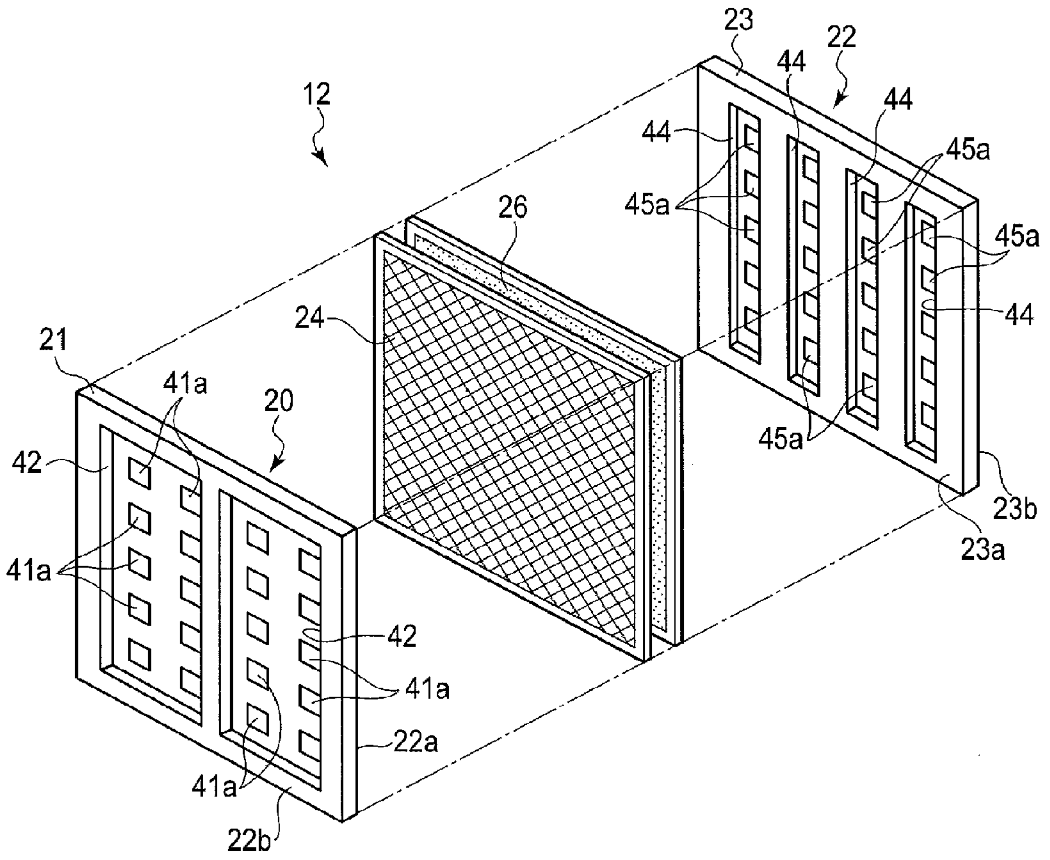
26b
24b

F I G. 11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45a
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45a
45a
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41a
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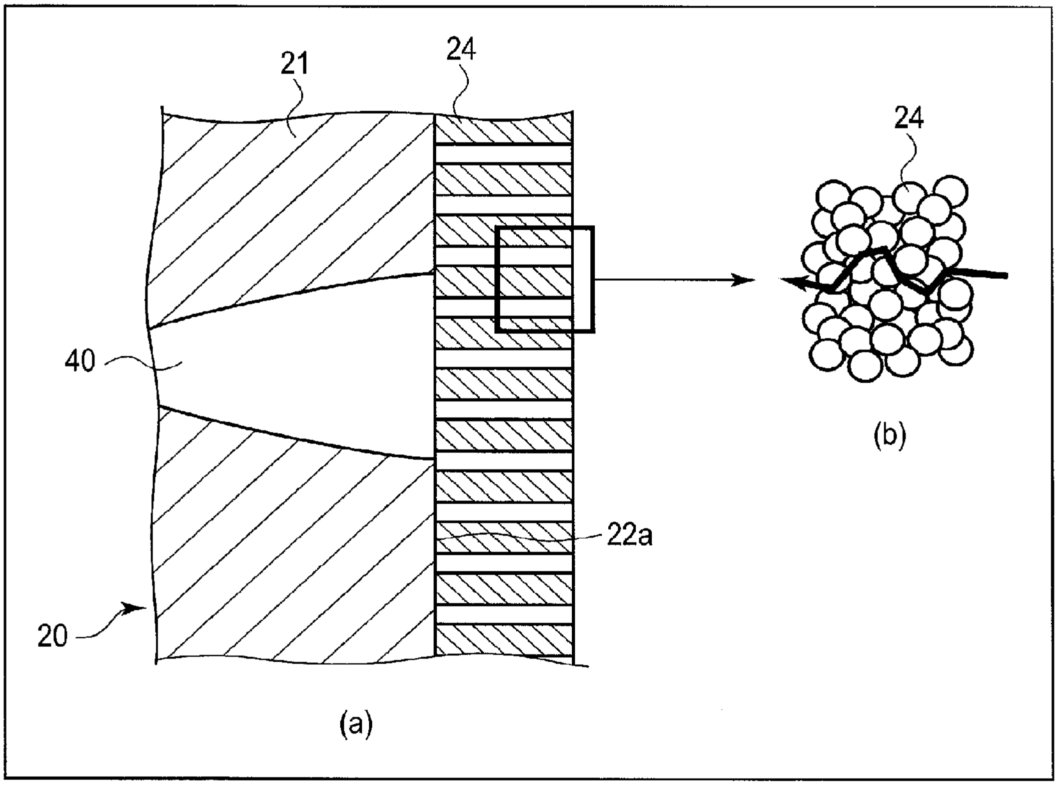
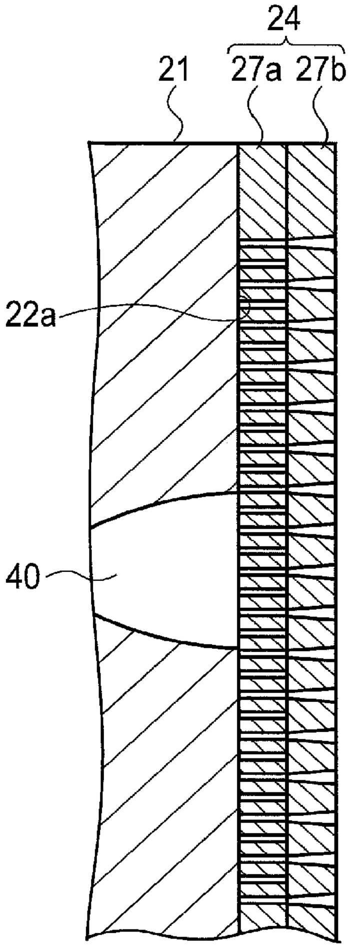
22a
41a
22b

FIG. 12



F I G. 13



F I G. 14

ELECTRODE UNIT, ELECTROLYTIC CELL COMPRISING ELECTRODE UNIT AND ELECTROLYTIC DEVICE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a Continuation application of PCT Application No. PCT/JP2015/056547, filed Mar. 5, 2015 and based upon and claiming the benefit of priority from Japanese Patent Application No. 2014-192015, filed Sep. 19, 2014, the entire contents of all of which are incorporated herein by reference.

FIELD

[0002] Embodiments described herein relate generally to an electrode unit, an electrolytic cell comprising the electrode unit and an electrolytic device.

BACKGROUND

[0003] In recent years, an electrolytic device for electrolyzing water and producing electrolyzed water which has various functions, such as ionized alkaline water, ozone water or aqueous hypochlorous acid has been provided. Of the electrolyzed water, aqueous hypochlorous acid has excellent sterilizing power and also is safe to human health; therefore it has been approved as a food additive.

[0004] As an electrolytic device, an electrolyzed-water production device comprising, for example, a three-chamber electrolytic cell is proposed. The inside of the electrolytic cell is divided into three chambers, namely, an intermediate chamber, and also an anode chamber and a cathode chamber located on both side of the intermediate chamber. The anode chamber and the cathode chamber are provided with an anode and a cathode, respectively. As the electrodes, a porous-structure type is employed, in which a great number of pores are made by processing such as expanding, etching or punching in a metal plate matrix.

[0005] In this type of electrolytic device, for example, salt water is supplied to the intermediate chamber, and water is supplied to the anode and cathode chambers. The salt water in the intermediate chamber is electrolyzed by the cathode and the anode. In this manner, aqueous hypochlorous acid is produced from gaseous chlorine produced by the anode. Aqueous sodium hydroxide is produced in the cathode chamber. The produced hypochlorous acid is used as sterilizing water. The aqueous sodium hydroxide is used as a cleaning solution.

[0006] In the three-chamber electrolytic cell, the anion-exchange membrane is degraded easily by chlorine or hypochlorous acid. When the electrode having a porous configuration adheres tightly to the ion-exchange membrane (electrolyte membrane), stress is easily concentrated on the edge portion of the pores of the electrode. Thus, the diaphragm formed of, for example, a thin electrolyte membrane which is weak mechanically, is deteriorated easily. In consideration of this factor, the following technique is suggested. To reduce the degradation of the electrode by chlorine, non-woven fabric having overlaps or slits is inserted between the electrode having a porous configuration and the electrolyte membrane.

[0007] However, if a porous membrane such as nonwoven fabric is inserted between the electrode and the electrolytic membrane, stress is applied to the porous membrane, causing variation in thickness in the porous membrane. In other words, the thickness of the porous membrane becomes uneven. The porous membrane of an uneven thickness causes irregular electrolytic reaction, resulting in reduction of the reactivity of the electrolytic device or degradation of the electrolytic membrane.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. **1** is a sectional view of an electrolytic device according to a first embodiment.

[0009] FIG. **2** is a sectional view showing an electrode unit of the electrolytic device according to the first embodiment.

[0010] FIG. **3** is an exploded perspective view of the electrode unit.

[0011] FIG. **4** is a sectional view showing a manufacturing process of an electrode.

[0012] FIG. **5** is a sectional view of an electrolytic device according to a second embodiment.

[0013] FIG. **6** is a perspective view of the electrode unit according to the second embodiment.

[0014] FIG. **7** is a sectional view of an electrode unit of an electrolytic device according to a third embodiment.

[0015] FIG. **8** is a perspective view of an electrode unit according to a fourth embodiment.

[0016] FIG. **9** is a sectional view of an electrolytic device according to a fifth embodiment.

[0017] FIG. **10** is a sectional view of an electrolytic device according to a sixth embodiment.

[0018] FIG. **11** is a sectional view of an electrode unit according to the third embodiment.

[0019] FIG. **12** is a perspective view of a first electrode and a second electrode according to a modification.

[0020] FIG. **13** is a sectional view schematically showing a porous membrane containing inorganic oxide and including pores formed in a planarly or three-dimensionally irregular manner.

[0021] FIG. **14** is a sectional view schematically showing a porous membrane consisting of a multi-layered film.

DETAILED DESCRIPTION

[0022] Various embodiments will be described in detail with reference to drawings. In general, according to one embodiment, an electrolytic device comprises an electrode unit. The electrode unit comprises: a first electrode including a first surface; a second surface located on an opposite side to the first surface, a plurality of first pores opened in the first surface, a plurality of second pores opened in the second surface and having an opening area greater than that of the first pores, and a plurality of first pores communicating with a respective one of the second pores; a second electrode opposing the first surface of the first electrode; and a continuous porous membrane interposed between the first electrode and the second electrode, so as to cover the first surface of the first electrode.

[0023] Throughout the embodiments, common structural members are designated by the same reference symbols, and the explanation thereof will not be repeated. Further, the drawings are schematic diagrams designed to assist the reader to understand the embodiments easily. Thus, there may be sections where the shape, dimensions, ratio, etc. are different from those of the actual devices, but they can be re-designed as needed with reference to the following explanations and publicly known techniques. For example, the electrodes are illustrated in plane in these figures, but they may be curved or formed in cylindrical according to the shape of the respective electrode units.

First Embodiment

[0024] FIG. **1** is a diagram briefly showing an electrolytic device according to the first embodiment. The electrolytic device **10** comprises, for example, a two-chamber electrolytic cell **11**, and an electrode unit **12** provided in the electrolytic cell **11**. The electrolytic cell **11** is formed into a flat rectangular box, the inside of which is divided by an electrode unit into two compartments, namely, an anode chamber **16** and a cathode chamber **18** by a dividing wall **14** and electrode unit **12**.

[0025] The electrode unit **12** comprises a first electrode (anode) **20** located in the anode chamber **16**, a second electrode (a counterelectrode or a cathode) **22** located in the cathode chamber **18**, and a porous membrane **24** and a diaphragm provided between the first and second electrodes.

[0026] The electrolytic device **10** comprises a power supply **30** to drive the first and second electrodes **20** and **22** of the electrode unit **12**, an ammeter **32**, a voltmeter **34** and a control device **36** that controls the members. A flow channel for liquid may be provided in the anode chamber **16** and the cathode chamber **18**. For example, a pipe or a pump for supplying liquid from outside or discharging liquid may be connected to the anode chamber **16** and the cathode chamber **18**. A porous spacer may be provided between the electrode unit **12** and the anode chamber **16** or the cathode chamber **18**.

[0027] Next, the electrode unit **12** will be described in detail. FIG. **2** is a sectional view of the electrode unit. FIG. **3** is an exploded perspective view of the electrode unit.

[0028] As shown in FIGS. **2** and **3**, the first electrode **20** has a porous structure in which numerous through-holes are formed in a matrix **21** of, for example, a rectangular metal plate. The matrix **21** includes a first surface **21***a* and a second surface **21***b* opposing and substantially parallel to the first surface **21***a*. The interval between the first surface **21***a* and the second surface **21***b*, in other words, the thickness of the matrix **21**, is defined as T**1**. The first surface **21***a* opposes the porous membrane **24** and the second surface **21***b* opposes the anode chamber **16**.

[0029] A plurality of first pores **40** of, for example, a square shape, are formed in the first surface **22***a* of the matrix **21** to open on the first surface **22***a*. Moreover, a plurality of second pores **42** are formed in the second surface **22***b* to open on the second surface **22***b*. The opening area of the second pores **42** is greater than that of the first pores **40**. The first pores **40** made on the porous membrane **24** side, have a dimension R**1** of the opening, which is less than a dimension R**2** of the openings of the second pores **42** of, for example, a square shape. Further, the first pores **40** are more in number than the second pores **42**. The depth of the first pores **40** is T**2** and the depth of the second pores **42** is T**3**, and T**2**+T**3**=T**1**. In this embodiment, the holes are made such that T**2**<T**3**.

[0030] In this embodiment, the second pores **42** are formed into, for example, a square shape to be arranged in a matrix on the second surface **22***b*. The circumferential wall which defines each second pore **42** may be formed to have a tapered surface **42***a* or curved surface so that the hole enlarges toward the second surface **22***b* side from the bottom of the hole to the opening. The interval between adjacent second pores **42**, that is, the width of a linear portion **60***a* of the electrode is set to W**2**. Note that the second pores **42** are not limited to a rectangular shape, but may take various other forms. Moreover, the second pores **42** may not necessarily be arranged regularly, but may be at random.

[0031] The opening diameter of the first pores **40** is preferably less in order to make the pressure uniform. However, the first pores **40** need to be large to the extent that substance diffusion can be prevented. In case of a square, the length of each side of the opening is preferably 0.1 to 2 mm, and is more preferably 0.3 to 1 mm. The opening may take a variety of forms such as a square, a rectangle, a rhomboid, a circle and an ellipse, and the vertices of a square, a rectangle or a rhomboid may be rounded. The opening area is preferably 0.01 to 4 mm^2 in the same manner as the above-described square. The opening area is more preferably 0.1 to 1.5 mm^2. The opening area is further preferably 0.2 to 1 mm^2. The ratio of the opening area to the electrode area including the opening (in other words, the opening ratio) is preferably 0.05 to 0.5, and is more preferably 0.1 to 0.4, and is further preferably 0.15 to 0.3. If the opening ratio is excessively less, outgassing is difficult. If the opening ratio is excessively great, electrode reaction is inhibited.

[0032] The first pores **40** are formed into, for example, a square shape and are arranged in a matrix on the first surface **21***a*. The circumferential wall which defines each first pore **40** may be formed to have a tapered surface **40***a* or curved surface so that the dimension enlarges from the bottom of the hole to the opening, in other words, to the first surface **22***a*. In this embodiment, a plurality, for example, nine of first pores **40** oppose a respective second pore **42** and communicate therewith to be made all the way through the matrix **21**. An interval W1 between adjacent first pores **40** is set so as to be less than an interval W2 between second pores **42**. With this structure, the number density of the first pores **40** in the first surface **21***a* is sufficiently greater than that of the second pores **42** in the second surface **21***b*.

[0033] Various shapes may be employed for each second pore **42**, such as a square, a rectangle, a rhomboid, a circle or an ellipse. The opening dimension of each second pore **42** is preferably great in order to facilitate outgassing. However, if the opening dimension is great, the electrical resistance is increased. Therefore, the second pores **42** cannot be significantly enlarged. In the case of the square opening, one side is preferably 1 to 40 mm, more preferably 2 to 30 mm, and further preferably 3 to 20 mm. The opening may take a variety of forms such as a square, a rectangle, a rhomboid, a circle and an ellipse, while the opening area is preferably 1 to 1600 mm^2 in the same manner as the above-described square. The opening area of the second pores **42** is more preferably 4 to 900 mm^2, and is further preferably 9 to 400 mm^2. For example, the opening may be shaped as a rectangle or an ellipse which is long in one direction so as to connect an end and the other end of the electrode.

[0034] For the matrix **21** of the first electrode **20**, a valve metal such as titanium, chromium or aluminum, or an alloy of these, or a conductive metal can be used. Out of these materials, titanium is preferable. It may be desirable, depending on the electrolytic reaction, to form an electrolytic catalyst (catalyst layer) on the first surface and the second surface of the electrode. When used as an anode, it is desirable to use a precious metal catalyst such as platinum or an oxide catalyst such as iridium oxide, as the matrix itself of the electrode. The amount of electrocatalyst per unit area on one surface of the electrode may differ from that on the other surface thereof. In this manner, for example, a side reaction may be prevented.

[0035] Further, the first pores **40** may not necessarily be arranged regularly, but may be at random. Furthermore, all the first pores **40** may not necessarily communicate with the second pores **42**, but there may be some first pores not communicating with a second pore **42**. Thus, some first pores **40** may not communicate with the anode chamber **16**. For example, as shown in FIG. **12**, the first pores **40** and **44** may be rectangles extending from near one end of the electrode to near the other end, within which a plurality of openings **41***a* and **45***a* communicating with the second pores **42** and **46** are arranged at certain interval. Only some of the first pores **40** and **44** may communicate with the second pores **42** and **44**. The first pores **40** and **44** which do not communicate with the second pores **42** and **44** can increase the electrode area.

[0036] Preferably, 85% or more of all of the first pores **40** and **44** have an opening area of 0.01 to 4 mm^2. More preferably, 90% or more, and further preferably, 95% or more of all of the first pores **40** have an opening area of 0.01 to 4 mm^2.

[0037] The first electrode **20** can be manufactured by, for example, an etching method using a mask. FIG. **4** briefly shows the manufacturing method thereof. As shown in FIGS. **4**(*a*) and (*b*), one flat matrix **21** is prepared. Resist films **50***a* and **50***b* are applied to the first and second surfaces **22***a* and **22***b* of the matrix **21**. Then, as shown in FIG. **4**(*c*), the resist films **50***a* and **50***b* are exposed using an optical mask (not shown) and thus etching masks **52***a* and **52***b* are formed, respectively. As shown in FIG. **4**(*d*), wet etching is applied to the first and second surfaces **22***a* and **22***b* of the matrix **21** via the masks **52***a* and **52***b* with solution. In this manner, a plurality of first pores **40** and a plurality of second pores **42** are formed. Subsequently, the first electrode **20** is obtained by removing the masks **52***a* and **52***b*.

[0038] The shape of the tapered or curved surface of the first and second pores **40** and **42** can be controlled based on the material of the matrix **21** and etching conditions. The depth of the first pores **40** is T2, and the depth of the second pores **42** is T**3**. As stated above, the first and second pores are formed such that T2<T**3**. In etching, both surfaces of the matrix **21** may be etched at the same time, or may be etched separately. The type of etching is not limited to wet etching. For example, dry etching may be employed. Moreover, not only etching but also processing by laser, precision cutting or the like may be employed to manufacture the first electrode **20**.

[0039] As shown in FIGS. **1** to **3**, in this embodiment, the second electrode (counterelectrode) **22** is structured in the same manner as the first electrode **20**. More specifically, the second electrode **22** has a porous configuration in which a large number of through-holes are formed in a matrix **23** made of, for example, a rectangular metal plate. The matrix **23** includes a first surface **23***a* and a second surface **23***b* opposing and substantially parallel to the first surface **23***a*. The first surface **23***a* oppose a diaphragm **26**. The second surface **23***b* opposes the cathode chamber **18**.

[0040] A plurality of first pores **44** are formed in the first surface **23***a* of the matrix **23** to open on the first surface **23***a*. Further, a plurality of second pores **46** are formed in the second surface **23***b* to open on the second surface **23***b*. The opening area of the first pores **42** on the diaphragm **26** is less than that of the second pores **44**. Further, the first pores **44** are more in number than the second pores **46**. The depth of the first pores **44** is less than that of the second pores **46**.

[0041] A plurality, for example, nine of first pores **44** are provided to oppose one second pore **46**. Each of these first pores **44** communicates with the second pore **26** so as to be made through the matrix **23**. The interval between adjacent first pores **44** is set so as to be less than the interval between the second pores **46**. With this structure, the number density of the first pores **44** on the first surface **23***a* is sufficiently greater than that of the second pores **46** on the second surface **23***b*.

[0042] The porous membrane **24** and the diaphragm **26** are interposed between the first surface **22***a* of the first electrode **20** and the first surface **23***a* of the second electrode **22**. The continuous porous membrane **24** is formed in, for example, a rectangular shape so as to have dimensions substantially equal to those of the first electrode **20**, and opposes the whole first surface **21***a*. As the porous membrane **24**, for example, a nonwoven fabric, cloth or a porous membrane which is formed by a sol-gel method can be used, and various materials may be used for the porous membrane. The porous membrane needs to be chemically stable. In particular, it needs stability to, especially, chlorine, hypochlorous acid or oxygen, or resistance to acid or alkali. Further, when used to process foods, for example, the following requirements should be met. That is, when it is a polymer, monomers or the like must not dissolve at amount determined by the law or more, or when it is an inorganic material, heavy metal ion must not dissolve at amount determined by the law or more. Mechanically, when the porous membrane is solely used without an undercoat member, it is important for the membrane to be handled easily, and therefore the thickness thereof is preferably 20 to 500 μm. If the porous membrane is formed directly on an electrode, it may be thin, but in order for the membrane to exhibit its properties, the thickness is preferably 50 nm or greater. Of these porous membranes, a polymer membrane containing a fluorine atom or a chlorine atom in its main chain, glass cloth or a membrane including irregular continuous pores and containing inorganic oxide, is especially chemically stable and preferable. As the polymer membrane, Teflon is particularly preferable. Hydroxide, alkoxide, oxyhalide or hydrate may be contained in the inorganic oxide. When the inorganic oxide is prepared by the hydrolysis of metal halide or metal alkoxide, a composite thereof may be easily obtained though it depends on the temperature of the subsequent treatment. The polymer membrane, glass cloth and inorganic oxide may be combined, and for example, the polymer membrane and glass cloth may be covered by an inorganic oxide. As shown in FIG. **13**, if an inorganic oxide film having irregular pores in a plane or in a three-dimensional manner is used as the porous membrane **24**, it may also function as a diaphragm. In other words, the diaphragm **26** may be omitted.

[0043] As shown in FIG. **14**, for the porous membrane **24**, a multilayer film including a plurality of porous membranes **27***a* and **27***b* having different pore diameters may be used. In this case, if the pore dimension of the porous membrane **27***b* located on the diaphragm **26** side is set greater than that of the porous membrane **27***b* located on the first electrode **20** side, migration of ions is more facilitated, and the stress concentration due to the pores of the electrode can be reduced. This is because as the opening on the diaphragm **26** side is greater, the ion migration by diffusion becomes easier. When the first electrode **20** is used for the anode, a positive potential is applied. Therefore, even if the pore diameter on the first electrode **20** side is less, anions are easily attracted to the first electrode **20**. If the pore diameter on the electrode **20** side is great, the produced chlorine or like is easily diffused to the porous membrane **24** side.

[0044] The pore diameter on the surface of the porous membrane **24** can be measured by a high-resolution scanning electron microscope (SEM). The pores inside the porous membrane can be measured by cross-sectional SEM observation.

[0045] As shown in FIGS. **2** and **3**, the diaphragm **26** is formed into, for example, a rectangular shape with dimensions substantially equal to those of the first electrode **20**, and also provided between the first surface **23***a* of the electrode **22** and the porous membrane **24**. The diaphragm **26** is tightly attached to the entire first surface **23***a* of the second electrode **22**, and further to the porous membrane **24**.

[0046] The diaphragm **26** located between the first and second electrodes **20** and **22** is a film which allows ions and/or liquid to pass therethrough. For the diaphragm **26**, various electrolyte membranes and porous membranes having nanopores may be used. For the electrolyte membrane, a polymer electrolyte membrane, for example, a cation-exchange solid polymer electrolyte membrane, more specicially, a cation-exchange membrane, an anion-exchange membrane or a hydrocarbon-based film may be used. Examples of the cation-exchange membrane are NAFION 112, 115 and 117 (trademark of E. I. du Pont de Nemours & Co.), Flemion (trademark of Asahi Glass Co., Ltd.), ACIPLEX (trademark of Asahi Chemical Co., Ltd.) and GOA SELECT (trademark of W. L. Goa and associates co.). An example of the anion-exchange membrane is A201 of Tokuyama, Inc. Usable examples of the porous membranes having nanopores are porous ceramics such as porous glass, porous alumina, porous titania and porous zeolite, and porous polymers such as porous polyethylen, porous propylene, porous teflon and porous polyimide.

[0047] The first electrode **20**, the porous membrane **24** and the second electrode **22** having the above-described structures are brought into contact with each other by pressing them in a state where the porous membrane **24** is interposed between the first electrode **20** and the second electrode **22**. In this manner, the electrode unit **12** is obtained.

[0048] As shown in FIG. **1**, the electrode unit **12** is provided in the electrolytic cell **11** and is attached to the dividing wall **14**. The electrolytic cell **11** is divided into the anode chamber **16** and the cathode chamber **18** by the dividing wall **14** and the electrode unit **12**. Thus, the electrode unit **12** is disposed in the electrolytic cell **11** so that the direction where the components which constitute this are in contact with each other is, for example, horizontal. The first electrode **20** of the electrode unit **12** faces the anode chamber **16**. The second electrode **22** faces the cathode chamber **18**.

[0049] In the electrolytic device **10**, both poles of the power supply **30** are electrically connected to the first electrode **20** and the second electrode **22**. The power supply **30** applies a voltage to the electrode unit **12** under the control of the control device **36**. The voltmeter **34** is electrically connected to the first electrode **20** and the second electrode **22** and detects the voltage applied to the electrode unit **12**. The detection data is supplied to the control device **36**. The ammeter **32** is connected to the voltage application circuit of the electrode unit **12** and detects the current flowing in the electrode unit **12**. The detection data is supplied to the control device **36**. The control device **36** controls the application of voltage or load for the electrode unit **12** by the power supply **30** based on the detected data in accordance with the program stored in the memory. The electrolytic device **10** applies a voltage or load between the first electrode **20** and the second electrode **22** in a state where the substance for reaction is supplied to the anode chamber **16** and the cathode chamber **18**. In this manner, the electrochemical reaction for electrolysis is advanced. The electrolytic device **10** of the present embodiment should preferably electrolyze an electrolyte containing chloride ions.

[0050] According to the electrolytic device and the electrode unit having the above-described structure, in the first electrode **20**, the diameter (opening area) of the first pores **40** formed in the first surface **22***a* on the porous membrane **24** side is made less than that of the second pores **42**. Thus, the number density thereof is increased. This structure allows the reduction in the concentration of stress applied from the first electrode **20** side to the porous membrane **24**. As a continuous membrane, the porous membrane **24** is brought into contact with the whole first surface **21***a* of the first electrode **20**. Thus, the holes of the first electrode **20** are covered by the porous membrane **24**. The distance between the first electrode **20** and the diaphragm **26** can be easily maintained equally over the whole surface. That is, distribution in the thickness of the porous membrane **24** can be prevented and it becomes possible to maintain the thickness of the porous membrane **24** uniformly. This structure enables the electrolytic reaction to occur uniformly, thereby improving the reaction efficiency of the electrolytic device and preventing the degradation of the electrolyte membrane.

[0051] Further, the first electrode **20** is formed to have the first pores **40** with a tapered or curved shape which enlarges towards the first surface side of the electrode. With this structure, the contact angle between the first pores **40** and the porous membrane **24** is obtuse, thereby making it possible to further reduce the concentration of stress on the porous membrane **24** from the first electrode **20** side. Note that the first surface **22***a* on the porous membrane **24** side of the first electrode **20** is preferably substantially flat except for recess portions. The recess portions may be the first pores described above or recessed sections which will be described later.

[0052] When the opening area of the second pores **42** formed in the second surface **22***b* of the first electrode **20** is increased and the number density is reduced, width W2 of the linear portions between the second pores **42** can be made sufficiently great. Thus, the mechanical strength of the first electrode **20** can be maintained high and the electric resistance can be reduced.

[0053] In the first embodiment having the above-described structures, it is possible to obtain a long-life, high-reaction-efficiency electrode unit and electrolytic device.

[0054] Note that in the first embodiment, the second electrode **22** has a porous structure with the first and second pores with different diameters, but it is not limited to this. For example, a plate electrode without a through-hole may be employed. Or such an electrode may be employed as well, that an electrode substrate is processed to have through-holes of the same diameter on the first surface and the second surface. The second electrode **22** and the diaphragm **26** may be in contact with each other, or a separate structural member may be interposed therebetween.

[0055] Next, an electrolytic cell and an electrolytic device according to another embodiment will be described. Note that in the other embodiments described below, the same reference symbols are given to the same structural elements as the first embodiment above, and the detailed explanations thereof are omitted. The portions different from those of the first embodiment will be mainly discussed.

Second Embodiment

[0056] FIG. **5** is a sectional view showing an electrode unit of an electrolytic device according to the second embodiment and FIG. **6** is a perspective view of an electrode.

[0057] According to the second embodiment, in the electrode unit **12**, the first surface **22***a* of the first electrode **20** is formed flat, and the first pores **40** described above are formed in the first surface **22***a* so as to be made through the matrix **21**. A plurality of recess portions **54** are formed in the first surface **22***a* of the first electrode **20**. In other words, the first electrode **20** includes recess portions **54**, which are recesses which are not made through the matrix **21**. The recess portions **54** are formed from, for example, continuous grooves extending between the first pores **40**. Or the recess portions **54** may be a great number of independent dot-like recesses.

[0058] The porous membrane **24** is tightly attached to the first surface **22***a* of the first electrode **20** and further opposes the first pores **40** and recess portions **54** to stop them.

[0059] The first surface **22***a* of the first electrode **20** is preferably flat except for the first pores **40** and the recess portions **54**. With the recess portions **54**, the electrode area can be increased, and also, flow channels for extracting the produced gas can be created. By forming the first surface **22***a* of the first electrode **20** substantially plate-like except for the recess portions **54**, the concentration of the stress on the porous membrane **24** can be further reduced. Although it vary depending on the thickness of the porous membrane **24**, the flatness of the first surface **22***a*, or the average surface roughness, is preferably 10% or less of the average thickness of the porous membrane **24**, more preferably, 5% or less, or further preferably, 2% or less. The average surface roughness can be examined by cross-sectional SEM observation.

[0060] Note that not only the first electrode **20**, but also the first surface **23***a* of the second electrode **22** may be provided with a plurality of recess portions.

Third Embodiment

[0061] FIG. **7** is a sectional view showing an electrode unit of an electrolytic device according to the third embodiment. According to the third embodiment, an electrically insulating film **56** which does not allow liquid to pass, is formed on at least a portion of the surface of the first electrode **20**. In the first electrode **20**, gas such as chlorine produced by the reaction is not easily discharged on the first surface **22***a*, which is widely in contact with the porous membrane **24** on the diaphragm **26** side. For this reason, the diaphragm **26** is deteriorated easily by the produced gas. Here, by covering the region of the first surface **22***a* where the first pores **40** are not formed with the insulating film **56**, the production of the reactive gas is suppressed in this region, and thus the deterioration of the diaphragm **26** can be prevented. In this embodiment, the insulating film **56** is formed on both the surfaces of the broad linear portion (width W**2**) of the first electrode **20**.

[0062] However, the reactive area of the first electrode **20** decreases by forming the insulating film **56**. Therefore, it is desirable to have the reaction of the first electrode **20** occur sufficiently in the portion where the produced gas can easily escape. Further, an electrically insulating film **57** may be formed for cover on the second surface **22***b* of the first electrode **20** located on the opposite side to the diaphragm **26**. When such an electrode unit **12** is used for a three-chamber electrolytic cell, a side reaction on the second surface **22***b* side can be reduced. Note that a portion of the insulating film may protrude in the sectional direction of the electrode.

Fourth Embodiment

[0063] FIG. **8** is a perspective view showing an electrode unit of an electrolytic device according to the fourth embodiment. According to the fourth embodiment, an interval W**3** between adjacent first pores **40** formed in the central portion of the electrode is set to be greater than an interval W**1** between those formed in the peripheral portion of the electrode. With this structure, the opening ratio (the ratio of the opening area to the electrode area including the opening area) of the central portion of the first electrode **20** is smaller than that of the peripheral portion of the first electrode **20**. Therefore, the electric resistance can be made lower in the central portion of the first electrode **20** than in the peripheral portion, thereby making it possible to reduce the voltage rise in the central portion of the electrode even in the case where power is supplied from the periphery of the electrode to the electrode. In order to reduce the opening ration, the opening area of the first pores **40** formed in the central portion of the first electrode **20** can be reduced by reducing the open area of those formed in the periphery as shown in FIG. **8**, or the number of pores can be reduced in the central portion.

Fifth Embodiment

[0064] FIG. **9** is a sectional view showing an electrolytic device according to the fifth embodiment. In the fifth embodiment, an electrolytic cell **11** of an electrolytic device **10** is structured as a one-chamber electrolytic cell comprising only one electrolytic chamber **17**. An electrode unit **12** is provided in the electrolytic chamber **17**. For example, a pipe or a pump for supplying an electrolyte from outside or discharging an electrolyte may be connected to the electrolytic chamber **17**.

[0065] In the one-chamber electrolytic cell **11**, a second electrode (counterelectrode) **22** of the electrode unit **12** preferably has a porous configuration in a manner similar to that of the first electrode **20**. The porous configuration enables the electrode area to be increased.

Sixth Embodiment

[0066] FIG. **10** is a sectional view showing an electrolytic device according to the sixth embodiment and FIG. **11** is a sectional view of an electrode unit in the electrolytic device.

[0067] As shown in FIG. **10**, an electrolytic device **10** comprises a three-chamber electrolytic cell **11** including an electrode unit **12**. The electrolytic cell **11** is formed into a flat rectangular box shape, the inside of which is divided into three chambers, specifically, an anode chamber **16**, a cathode chamber **18** and an intermediate chamber **19** formed between the electrodes, by a dividing wall **14** and the electrode unit **12**.

[0068] The electrode unit **12** comprises a first electrode (anode) **20** disposed in the anode chamber **16**, a second electrode (counterelectrode or cathode) **22** disposed in the cathode chamber **18**, two diaphragms **26***a* and **26***b* provided between the first and second electrodes, a porous membrane **24***a* interposed between the first electrode **20** and the diaphragm **26***a*, and a porous membrane **24***b* interposed between the second electrode **22** and the diaphragm **26***b*. The diaphragms **26***a* and **26***b* oppose each other with an intervening space such that they are parallel to each other. The intermediate chamber (electrolyte chamber) **19** which holds an electrolyte is formed between the diaphragms **26***a* and **26***b*. A holder **25** which holds an electrolyte may be provided in the intermediate chamber **19**. The first and second electrodes **20** and **22** may be connected to each other by a plurality of insulating bridges **60**.

[0069] The electrolytic device **10** comprises a power supply **30** which applies a voltage to the first and second electrodes **20** and **22** of the electrode unit **12**, an ammeter **32**, a voltmeter **34** and a control device **36** which controls these elements. A flow channel for liquid may be provided in the anode chamber **16** and the cathode chamber **18**. For example, a pipe or a pump for supplying liquid from outside or discharging liquid may be connected to the anode chamber **16** and the cathode chamber **18**. A porous spacer may be provided between the electrode unit **12** and the anode chamber **16** or the cathode chamber **18** depending on the case.

[0070] As shown in FIGS. **10** and **11**, in the electrode unit **12**, the first and second electrodes **20** and **22** are formed to have a porous configuration similar to that of the first embodiment discussed above. The continuous porous membrane **24** is formed in, for example, a rectangular shape so as to have dimensions substantially equal to those of the first electrode **20**, and opposes the whole first surface **21***a*. As the porous membranes **24***a* and **24***b*, for example, a nonwoven fabric, cloth or a porous membrane which is formed by a sol-gel method can be used, and various materials may be used for the porous membranes. Of these porous membranes, a polymer membrane containing a fluorine atom or a chlorine atom in its main chain, glass cloth or a membrane including irregular continuous pores and containing inorganic oxide, is especially chemically stable and preferable. If an inorganic oxide film having irregular pores is used as the porous membranes **24***a* and **24***b*, they can also function as diaphragms. The porous membranes **24** and **27** may be multilayer films of a plurality of porous membranes having different pore-diameters.

[0071] The diaphragm **26***a* is formed in, for example, a rectangular shape so as to have dimensions substantially similar to those of the first electrode **20**, and opposes the first surface **22***a* of the first electrode **20**. The porous membrane **24***a* is interposed between the first surface **22***a* of the first electrode **20** and the diaphragm **26***a*, and adheres tightly to the first electrode **20** and the diaphragm **26***a*.

[0072] The diaphragm **26***b* is formed in, for example, a rectangular shape so as to have dimensions substantially equal to those of the second electrode **22**, and opposes the first surface **23***a* of the second electrode **22**. The porous membrane **24***b* is interposed between the first surface **23***a* of the second electrode **22** and the diaphragm **26***b*, and adheres tightly to the second electrode **22** and the diaphragm **26***b*.

[0073] The diaphragms **26***a* and **26***b* are films which allow ions and/or liquid to pass therethrough. For the diaphragm **26**, various electrolyte membranes and porous membranes having nanopores may be used.

[0074] In the sixth embodiment having the above-described structure, effects similar to those of the first embodiment can be obtained. It is possible to obtain a long-life, high-reaction-efficiency electrode unit and electrolytic device.

[0075] Next, various examples and comparative example will be described.

Example 1

[0076] For the electrode matrix **21**, a flat titanium plate having a thickness (T**1**) of 0.5 mm is employed. This titanium plate is etched as shown in FIG. **4**. In this manner, an electrode is manufactured. In this electrode, a thickness T**2** of a region including the smaller-dimension first pores **40** (depth of the first pores) is 0.15 mm, and a thickness T**3** of a region including the larger-dimension second pores **42** (depth of the second pores) is 0.35 mm. The first pores **40** have a square shape whose vertices are rounded, and one side R**1** of the square obtained by extrapolating the straight line part is 0.57 mm. The second pores **42** have a square shape, and one side R**2** thereof is 2 mm. A width W**1** of a linear portion formed between adjacent first pores **40** is 0.1 mm and a width W**2** of a wide linear portion formed between adjacent second pores **42** is 1.0 mm.

[0077] The electrode matrix **21** is processed in advance in a 10-wt % oxalic acid aqueous solution at 80° C. for an hour. 1-butanol is added to iridium chloride ($IrCl_3.nH_2O$) to be adjusted to 0.25M (Ir) and the mixture is applied to the surface (first surface) of the electrode matrix **21** in which the first pores **40** are formed, followed by drying and burning. In this case, drying is performed at 80° C. for 10 minutes, and the burning is performed at 450° C. for 10 minutes. The above-described application, drying and burning are repeated five times. The electrode matrix made through this process is cut out such that the reactive electrode area can be 3 cm×4 cm. In this manner, the first electrode (anode) **20** is manufactured. The average coarseness of the flat portion of the first electrode **20** except for the recess portions is measured by AFM to be 1 μm.

[0078] Further, the second electrode (a counterelectrode, a cathode) **22** is produced by sputtering platinum onto the first surface of the electrode matrix in which the first pores are formed.

[0079] The electrode unit **12** shown in FIG. **11** is manufactured, using the first and second electrodes thus obtained. For the diaphragm **26***a*, an anion-exchange membrane, A201 of Tokuyama, Inc is employed, and for the diaphragm **26***b*, NAFION (trademark) 117 is employed. A glass cloth (75-μm-thick) is used for the porous membranes **24***a* and **24***b*. As the holder **25** which holds the electrolyte, porous polystyrene having a thickness of 5 mm is provided in the intermediate chamber (electrolyte chamber) **19**. The first and second electrodes, the porous membrane, the dividing wall and porous polystyrene are put and fixed together using silicone seal adhesive and a screw, to form the electrode unit **12**. Using this electrode unit **12**, the electrode unit **12** and the electrolyte device **10** shown in FIG. **10** are manufactured.

[0080] The anode chamber **16** and the cathode chamber **18** of the electrolytic cell **11** are each formed from a vinyl-chloride container in which a straight pathway is formed. The control device **36**, the power supply **30**, the voltmeter **34** and the ammeter **32** are provided. A pipe and a pump for supplying water to the anode and cathode chambers **16** and **18** are connected to the electrolytic cell **11**. Further, a saturated salt water tank, a pipe and a pump for circulating a saturated salt water to the holder (porous polystyrene) **25** of the electrode unit **12** are connected to the electrode unit. The electrolytic device **10** is operated for electrolysis at a voltage of 5V and a current of 1.5 A. Aqueous hypochlorous acid is produced on the anode **20** side, and aqueous sodium hydroxide is produced on the cathode **22** side. Even after continuous operation for

1000 hours, no substantial rise in voltage or change in product concentration is observed. Thus, a stable electrolytic treatment can be carried out.

Example 2

[0081] With a different mask used in the etching, a first electrode **20** is manufactured from an electrode matrix of 3×4 cm, having a central portion of 1×1.4 cm, where first pores **40** each having a square shape whose one side R**1** has a length of 0.7 mm are formed and a width W**1** of a linear portion is 0.2 mm. The second pores **42** have a square shape whose one side has a length of 2 mm. The second pore formed in the central portion included the first pores in an arrangement of 2×2. The other structures are the same as those of Example 1. On these conditions, the electrode unit **12** and the electrolytic device **10** are manufactured.

[0082] The electrolytic device **10** is operated for electrolysis at a voltage of 4.8 V and a current of 1.5 A. Aqueous hypochlorous acid is produced on the anode **20** side, and aqueous sodium hydroxide is produced on the cathode **22** side. Even after continuous operation for 1000 hours, no substantial rise in voltage or change in product concentration is observed. Thus, a stable electrolytic treatment can be carried out.

Example 3

[0083] As the porous membrane, a nonwoven fabric made from polyvinylidene chloride is used instead of the glass cloth. The other structures are the same as those of Example 1. On these conditions, the electrode unit **12** and the electrolytic device **10** are manufactured.

[0084] The electrolytic device **10** is operated for electrolysis at a voltage of 5.1 V and a current of 1.5 A. Aqueous hypochlorous acid is produced on the anode **20** side, and aqueous sodium hydroxide is produced on the cathode **22** side. Even after continuous operation for 1000 hours, no substantial rise in voltage or change in product concentration is observed. Thus, a stable electrolytic treatment can be carried out.

Example 4

[0085] As the porous membrane, a porous titanium oxide membrane including irregular pores is used instead of the glass cloth. The other structures are the same as those of Example 1. On these conditions, the electrode unit **12** and the electrolytic device **10** are manufactured.

[0086] The electrolytic device **10** is operated for electrolysis at a voltage of 5.2 V and a current of 1.5 A. Aqueous hypochlorous acid is produced on the anode **20** side, and aqueous sodium hydroxide is produced on the cathode **22** side. Even after continuous operation for 1000 hours, no substantial rise in voltage or change in product concentration is observed. Thus, a stable electrolytic treatment can be carried out.

Example 5

[0087] As the porous membrane, a nonwoven fabric made from Teflon is used instead of the glass cloth. The other structures are the same as those of Example 1. On these conditions, the electrode unit **12** and the electrolytic device **10** are manufactured.

[0088] The electrolytic device **10** is operated for electrolysis at a voltage of 5.0 V and a current of 1.5 A. Aqueous hypochlorous acid is produced on the anode **20** side, and aqueous sodium hydroxide is produced on the cathode **22** side. Even after continuous operation for 1000 hours, no substantial rise in voltage or change in product concentration is observed. Thus, a stable electrolytic treatment can be carried out.

Example 6

[0089] A first electrode **20** is manufactured as in Example 1 and electric-insulating polyvinyl chloride is applied selectively on a wide linear portion (having a width of W**2**) to form an insulating film by screen printing. The other structures are the same as those of Example 1. On these conditions, the electrode unit **12** and the electrolytic device **10** are manufactured.

[0090] The electrolytic device **10** is operated for electrolysis at a voltage of 5.3 V and a current of 1.5 A. Aqueous hypochlorous acid is produced on the anode **20** side, and aqueous sodium hydroxide is produced on the cathode **22** side. Even after continuous operation for 1000 hours, no substantial rise in voltage or change in product concentration is observed. Thus, a stable electrolytic treatment can be carried out.

Example 7

[0091] A second electrode (counterelectrode) **22** of a porous structure is manufactured as in Example 1. As the diaphragm **26**, a porous glass film (50-µm-thick) is employed. As the porous membrane **24**, a glass cloth (75-µm-thick) is employed. They are then put together using a silicone sealing material and screws to form an electrode unit **12**.

[0092] Using the electrode unit **12**, a one-chamber electrolytic cell **11** and an electrolyte device **10** shown in FIG. **9** are manufactured. A control device **36**, a power supply **30**, a voltmeter **34** and an ammeter **32** are provided. A pipe and a pump for supplying salt water to an electrolytic chamber **17** are provided. The electrolytic device **10** is operated for electrolysis at a voltage of 4.3 V and a current of 1.5 A to produce aqueous hypochlorous acid. Even after continuous operation for 1000 hours, no substantial rise in voltage or change in product concentration is observed. Thus, a stable electrolytic treatment can be carried out.

Example 8

[0093] As the porous membrane, a polyphenylene sulfide porous membrane coated with a film containing titanium oxide is employed instead of the glass cloth. The polyphenylene sulfide porous membrane coated with a film containing titanium oxide is used to also serve as the diaphragms **26***a* and **26***b*. The other structures are the same as those of Example 1. On these conditions, the electrode unit **12** and the electrolytic device **10** are manufactured.

[0094] The electrolytic device **10** is operated for electrolysis at a voltage of 4.8 V and a current of 1.5 A. Aqueous hypochlorous acid is produced on the anode **20** side, and aqueous sodium hydroxide is produced on the cathode **22** side. Even after continuous operation for 2000 hours, no substantial rise in voltage or change in product concentration is observed. Thus, a stable electrolytic treatment can be carried out.

Example 9

[0095] As the porous membrane, a glass-made nonwoven fabric (filter paper) coated with a film containing titanium oxide is employed instead of the polyphenylene sulfide porous membrane coated with a film containing titanium oxide. The other structures are the same as those of Example 8. On these conditions, the electrode unit **12** and the electrolytic device **10** are manufactured.

[0096] The electrolytic device **10** is operated for electrolysis at a voltage of 4.7 V and a current of 1.5 A. Aqueous hypochlorous acid is produced on the anode **20** side, and aqueous sodium hydroxide is produced on the cathode **22** side. Even after continuous operation for 2000 hours, no substantial rise in voltage or change in product concentration is observed. Thus, a stable electrolytic treatment can be carried out.

Example 10

[0097] As the porous membrane, a glass-made nonwoven fabric (filter paper) coated with a film containing zirconium oxide is employed instead of the polyphenylene sulfide porous membrane coated with a film containing titanium oxide. The other structures are the same as those of Example 8. On these conditions, the electrode unit **12** and the electrolytic device **10** are manufactured.

[0098] The electrolytic device **10** is operated for electrolysis at a voltage of 4.8 V and a current of 1.5 A. Aqueous hypochlorous acid is produced on the anode **20** side, and aqueous sodium hydroxide is produced on the cathode **22** side. Even after continuous operation for 2000 hours, no substantial rise in voltage or change in product concentration is observed. Thus, a stable electrolytic treatment can be carried out.

Example 11

[0099] As the porous membrane, a membrane further coated with a more precise film containing zirconium oxide on an electrode-side surface of the porous membrane is employed instead of the polyphenylene sulfide porous membrane coated with a film containing titanium oxide. The other structures are the same as those of Example 8. On these conditions, the electrode unit **12** and the electrolytic device **10** are manufactured.

[0100] This electrolytic device **10** is operated for electrolysis at a voltage of 4.9 V and a current of 1.5 A. Aqueous hypochlorous acid is produced on the anode **20** side, and aqueous sodium hydroxide is produced on the cathode **22** side. Even after continuous operation for 2000 hours, no substantial rise in voltage or change in product concentration is observed. Thus, a stable electrolytic treatment can be carried out.

Example 12

[0101] As the porous membrane, a membrane coated with a Teflon porous membrane further coated with a film containing zirconium oxide is employed instead of the polyphenylene sulfide porous membrane coated with a film containing titanium oxide. The other structures are the same as those of Example 8. On these conditions, the electrode unit **12** and the electrolytic device **10** are manufactured.

[0102] This electrolytic device **10** is operated for electrolysis at a voltage of 4.9 V and a current of 1.5 A. Aqueous hypochlorous acid is produced on the anode **20** side, and aqueous sodium hydroxide is produced on the cathode **22** side. Even after continuous operation for 2000 hours, no substantial rise in voltage or change in product concentration is observed. Thus, a stable electrolytic treatment can be carried out.

Example 13

[0103] For the electrode matrix **21**, a flat titanium plate having a thickness T**1** of 0.5 mm is employed. This titanium plate is etched as shown in FIG. **4** to manufacture an electrode. In this electrode, a thickness T**2** of a region including the smaller-dimension first pores **40** (depth of the first pores) is 0.15 mm, and a thickness T**3** of a region including the larger-dimension second pores **42** (depth of the second pores) is 0.35 mm. The first pores **40** have a rhomboid shape whose long diagonal is 0.69 mm and short diagonal is 0.4 mm. The second pores **42** have a rhomboid shape whose long diagonal line has a length of 6.1 mm and short diagonal line has a length of 3.5 mm. A width W**1** of a linear portion formed between adjacent first pores **40** is 0.15 mm and a width W**2** of a wide linear portion formed between adjacent second pores **42** is 1 mm. The other structures are the same as those of Example 1. On these conditions, the electrode unit **12** and the electrolytic device **10** are manufactured.

[0104] This electrolytic device **10** is operated for electrolysis at a voltage of 5.3 V and a current of 1.5 A. Aqueous hypochlorous acid is produced on the anode **20** side, and aqueous sodium hydroxide is produced on the cathode **22** side. Even after continuous operation for 1000 hours, no substantial rise in voltage or change in product concentration is observed. Thus, a stable electrolytic treatment can be carried out.

Example 14

[0105] For the electrode matrix **21**, a flat titanium plate having a thickness T**1** of 0.5 mm is employed. This titanium plate is etched as shown in FIG. **4** to manufacture an electrode. In this electrode, a thickness T**2** of a region including the smaller-dimension first pores **40** (depth of the first pores) is 0.15 mm, and a thickness T**3** of a region including the larger-dimension second pores **42** (depth of the second pores) is 0.35 mm. The first pores **40** have a square shape whose one side R**1** has a length of 0.57 mm. The second pores **42** have a rectangular shape whose long side has a length of 40 mm and short side has a length of 4 mm. A width W**1** of a linear portion formed between adjacent first pores **40** is 0.1 mm and a width W**2** of a wide linear portion formed between adjacent second pores **42** is 1.0 rum. The other structures are the same as those of Example 1. On these conditions, the electrode unit **12** and the electrolytic device **10** are manufactured.

[0106] This electrolytic device **10** is operated for electrolysis at a voltage of 5.8 V and a current of 1.5 A. Aqueous hypochlorous acid is produced on the anode **20** side, and aqueous sodium hydroxide is produced on the cathode **22** side. Even after continuous operation for 1000 hours, no substantial rise in voltage or change in product concentration is observed. Thus, a stable electrolytic treatment can be carried out.

Comparative Example 1

[0107] An electrolytic device is manufactured in a similar manner to that of Example 1 except that the continuous porous membrane is not employed in this example. This electrolytic device is operated for electrolysis at a voltage of 5 V and a current of 1.5 A. Aqueous hypochlorous acid is produced on the anode side, and aqueous sodium hydroxide is produced on the cathode side. After continuous operation for 1000 hours, a significant rise in voltage and a decrease in product concentration are observed. Thus, this device did not exhibit a long-term stability.

Comparative Example 2

[0108] An electrolytic device is manufactured by forming through-holes having a diameter of 1 mm in an electrode matrix by punching to have the same opening ratio as that of the electrode of Example 1. The other structures are the same as those of Example 1. On these conditions, the electrode unit and the electrolytic device are manufactured.

[0109] This electrolytic device is operated for electrolysis at a voltage of 5.2 V and a current of 1.5 A. Aqueous hypochlorous acid is produced on the anode side, and aqueous sodium hydroxide is produced on the cathode side. After continuous operation for 1000 hours, a significant rise in voltage and a decrease in product concentration are observed. Thus, this device did not exhibit a long-term stability.

[0110] The present invention is not limited to the embodiments and modifications described above but the constituent elements of the invention can be modified in various manners without departing from the spirit and scope of the invention. Various aspects of the invention can also be extracted from any appropriate combination of a plurality of constituent elements disclosed in the embodiments. For example, some constituent elements may be deleted in all of the constituent elements disclosed in the embodiments. Further, the constituent elements described in different embodiments may be combined arbitrarily.

[0111] For example, the first electrode and the second electrode are not limited to rectangular shapes, but various other forms may be selected. The first and second pores of the first electrode are not limited to square shapes, and may have various other shapes such as a rectangular, rhomboid, circular or elliptical shape. Further, the material of each structural component is not limited to that employed in the embodiments or examples discussed, but various other materials may be selected as needed. The electrolytic cell of the electrode device is not limited to a three-chamber type, but it may as well be applied to a two-chamber- or single-chamber type or any electrolytic cells with electrodes in general. The electrolytes and product are not limited to salt or hypochlorous acid, but may be developed into various electrolytes and products.

1: An electrode unit comprising:

a first electrode including: a first surface, a second surface located on an opposite side to the first surface, a plurality of first pores opened in the first surface, a plurality of second pores opened in the second surface and having an opening area greater than that of the first pores, a plurality of the first pores communicating with a respective one of the second pores;

a second electrode opposing the first surface of the first electrode; and

a continuous porous membrane arranged between the first electrode and the second electrode, so as to cover the first surface of the first electrode.

2: The electrode unit of claim **1**, wherein an opening area of the first pores opened in the first surface is 0.01 to 4 mm^2.

3: The electrode unit of claim **1**, wherein an opening area of the second pores opened in the second surface is 1 to 1600 mm^2.

4: The electrode unit of claim **1**, wherein a number density of the first pores per unit area is higher than that of the second pores per unit area.

5: The electrode unit of claim **1**, wherein a catalytic layer is formed on the first surface and the second surface of the electrode, and an amount of the catalytic layer per unit area differs from the first surface to the second surface.

6: The electrode unit of claim **1**, wherein the first pores are formed to have a tapered surface or a curved surface which widens towards the first surface.

7: The electrode unit of claim **1**, wherein the first electrode includes recess portions formed in the first surface, and the first surface is formed flat except for the first pores and the recess portions.

8: The electrode unit of claim **7**, wherein an average surface roughness of a flat portion of the first electrode is 10% or less of an average thickness of the porous membrane.

9: The electrode unit of claim **1**, wherein an opening ratio of first pores located in a central portion of the first electrode is less than an opening ratio of first pores located in a peripheral portion of the first electrode.

10: The electrode unit of claim **1**, further comprising: an electrically insulating film which inhibits liquid from passing therethrough and is provided on at least a portion of the first surface of the first electrode.

11: The electrode unit of claim **1**, wherein the second electrode has a porous structure including a plurality of through-holes.

12: The electrode unit of claim **1**, wherein the porous membrane is a polymer membrane containing a fluorine atom or a chlorine atom in a main chain thereof.

13: The electrode unit of claim **1**, wherein the porous membrane is a glass cloth.

14: The electrode unit of claim **1**, wherein the porous membrane is a membrane including in-planerly or three-dimensionally irregular pores and containing inorganic oxide.

15: The electrode unit of claim **1**, wherein the porous membrane is a multi-layer film in which a plurality of porous films having different pore diameters are stacked one on another.

16: The electrode unit of claim **1**, further comprising: a diaphragm provided between the first surface of the first electrode and the second electrode, which allows at least one of ion and liquid to pass therethrough, and

wherein the porous membrane is interposed between the first surface of the first electrode and the diaphragm.

17: The electrode unit of claim **1**, further comprising:

two diaphragms provided between the first electrode and the second electrode so as to oppose each other; and

an electrolyte holding structure located between the two diaphragms to hold electrolyte.

18: An electrolytic cell comprising: an electrolytic chamber and an electrode unit of claim **1**, provided in the electrolytic chamber.

19: An electrolytic device comprising:

an electrolytic cell including an electrolytic chamber;

an electrode unit of claim **1**, provided in the electrolytic chamber; and

a power supply which applies a voltage to the first electrode and the second electrode of the electrode unit.

20: The electrolytic device of claim **19**, wherein an electrolyte containing chloride ions is electrolyzed by the electrode unit.

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