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(54) **ELECTROCHEMICAL REACTION DEVICE**

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(57) **ABSTRACT**

An electrochemical reaction device comprises: an anode to oxidize water; an electrolytic solution flow path facing on the anode and through which an electrolytic solution containing the water flows; a cathode including: a porous conductive layer having first and second surfaces; and a reduction catalyst layer having a third surface disposed on the first surface and containing a reduction catalyst to reduce carbon dioxide; a separator between the anode and the cathode; a power supply connected to the anode and the cathode; and a flow path plate including: a fourth surface on the second surface; and a flow path facing on the second surface and through which the carbon dioxide flows. A ratio of an area of an overlap of the second surface and the flow path to an area of the second surface is 0.5 or more and 0.85 or less.

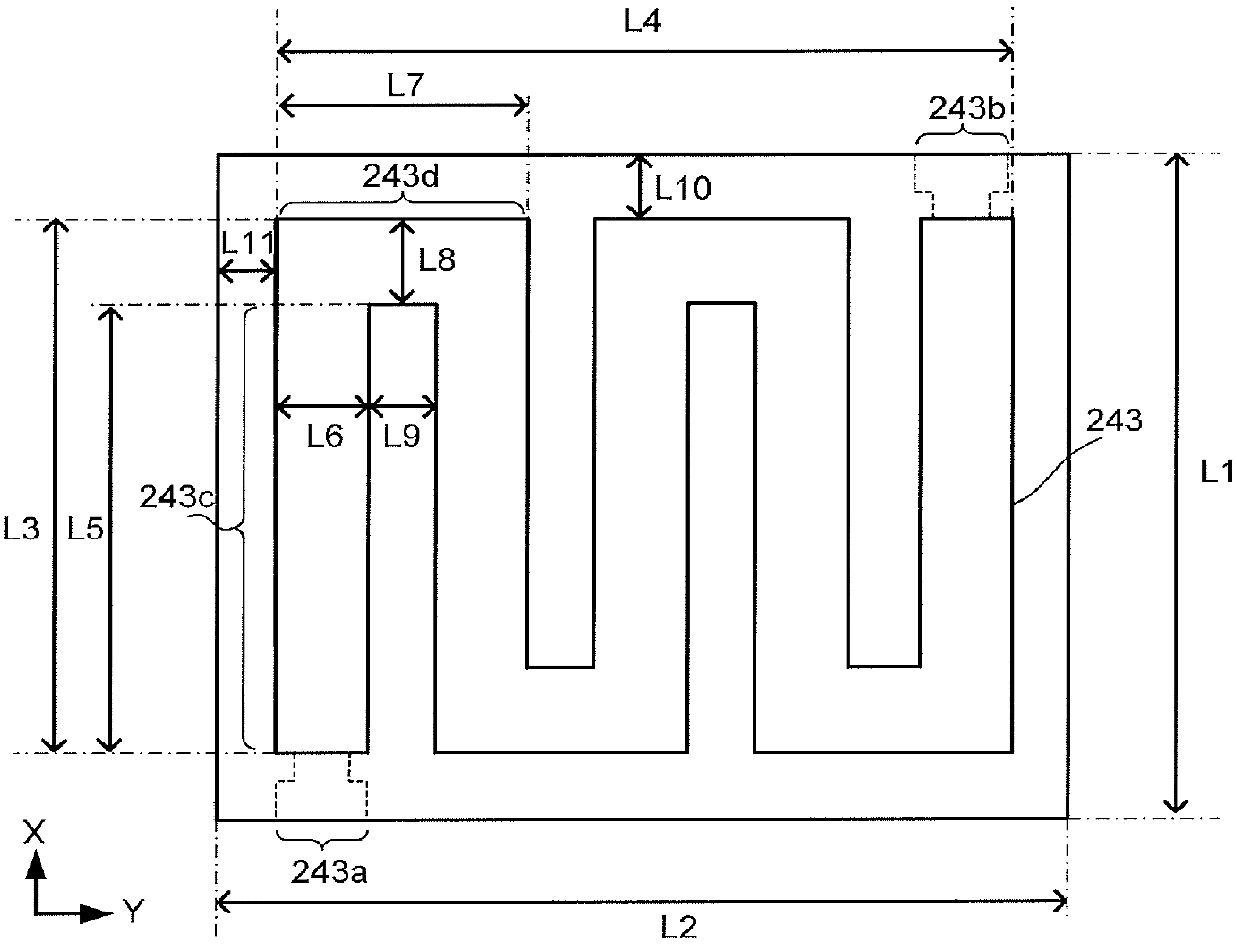


FIG.1

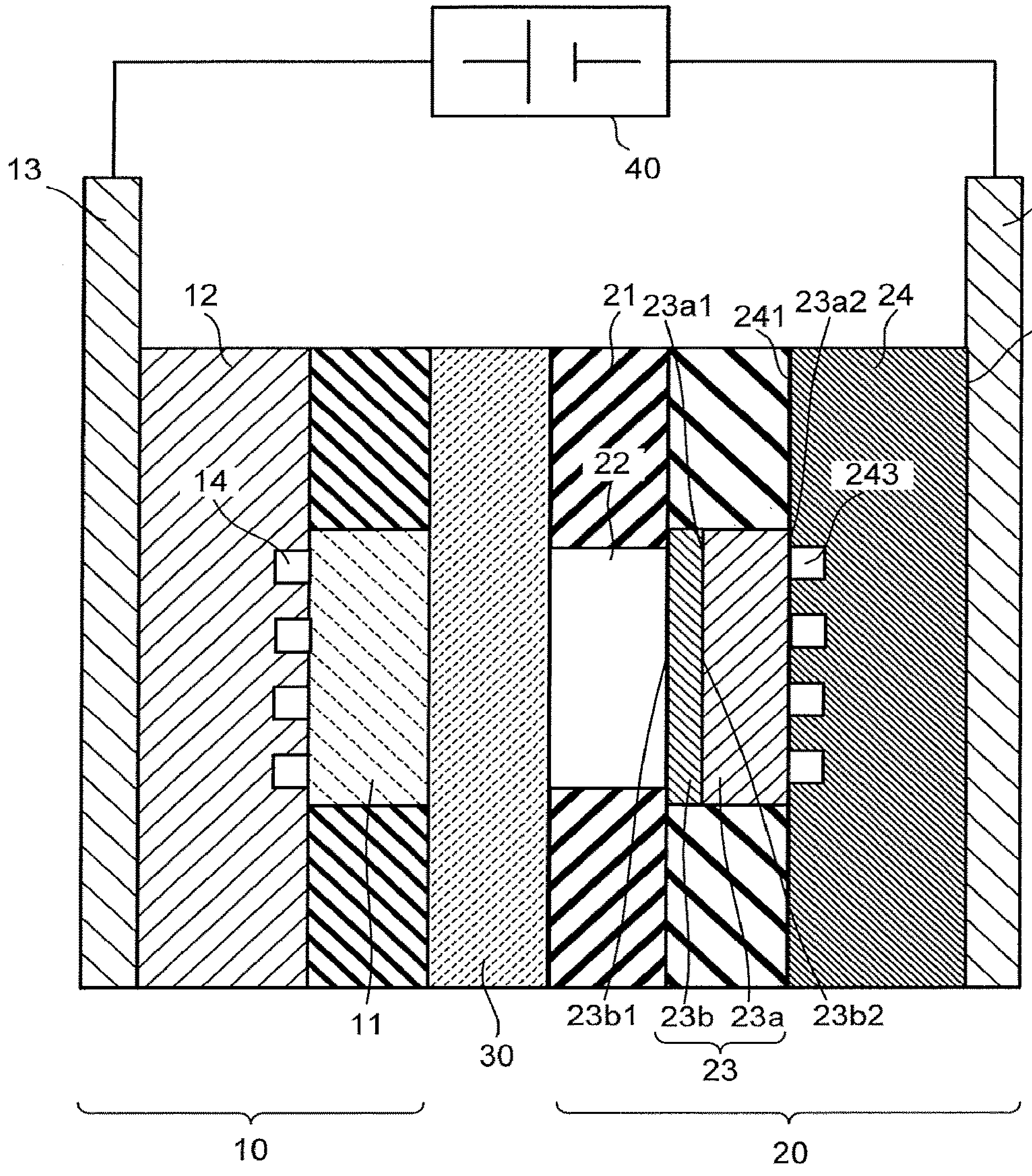

40
13
25
12
21
23a1
241
23a2
24
242
22
14
243
11
30
23b1
23b
23a
23b2
23
10
20

FIG.2

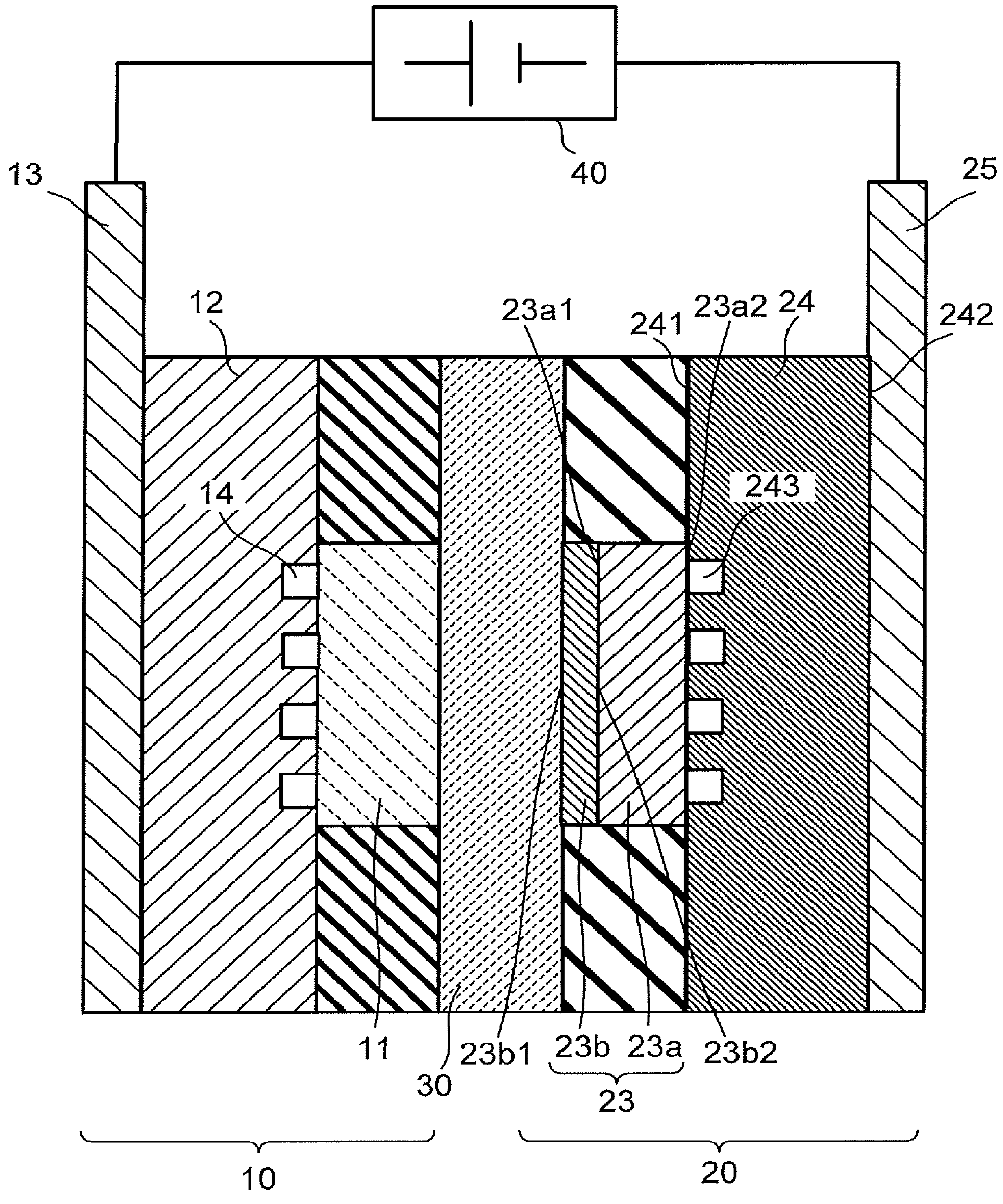

40
13
25
12
23a1
241
23a2
24
242
14
243
11
30
23b1
23b
23a
23b2
23
10
20

FIG.3

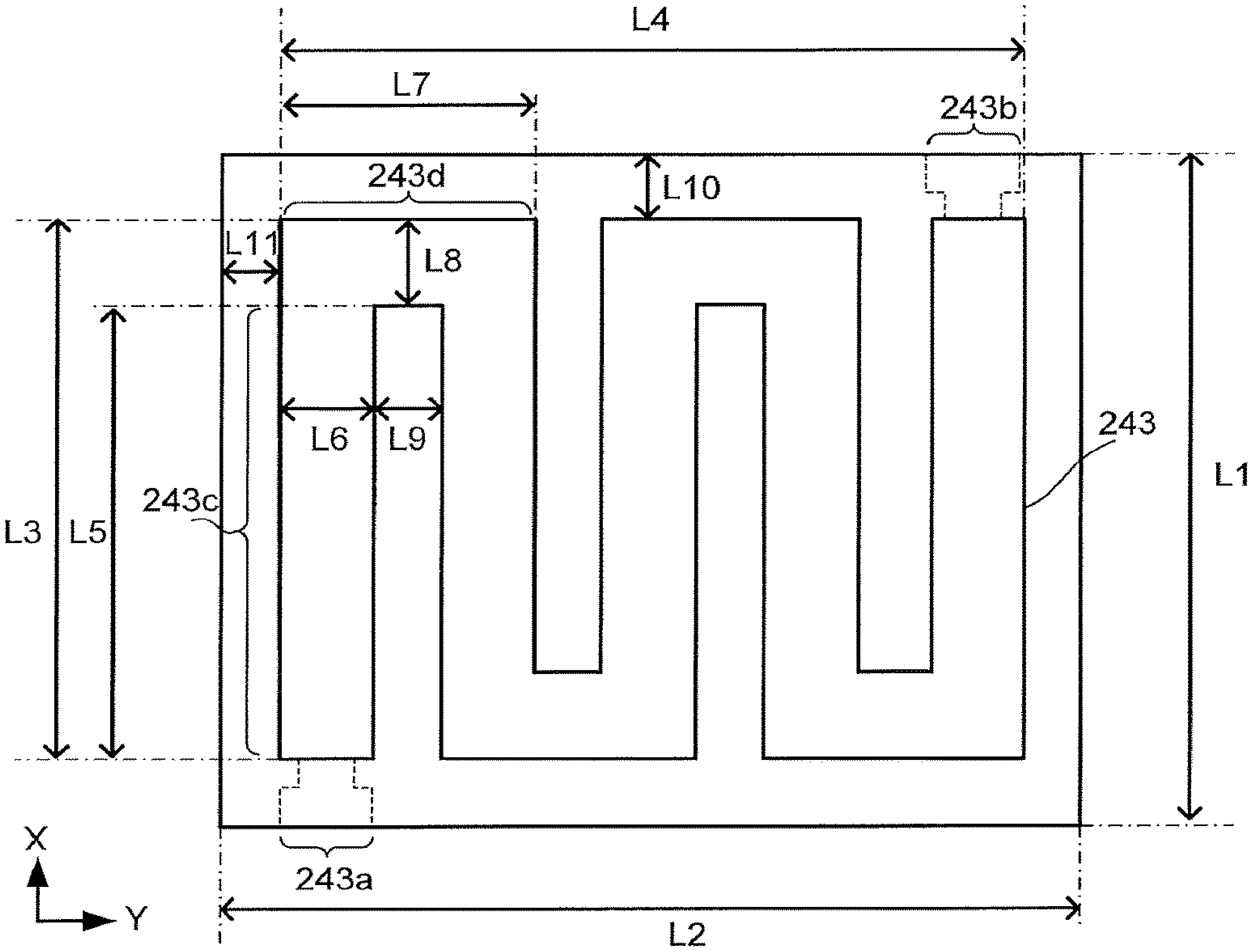

L4
L7
243b
243d
L10
L11
L8
L6
L9
243
L1
243c
L3
L5
X
Y
243a
L2

FIG.4

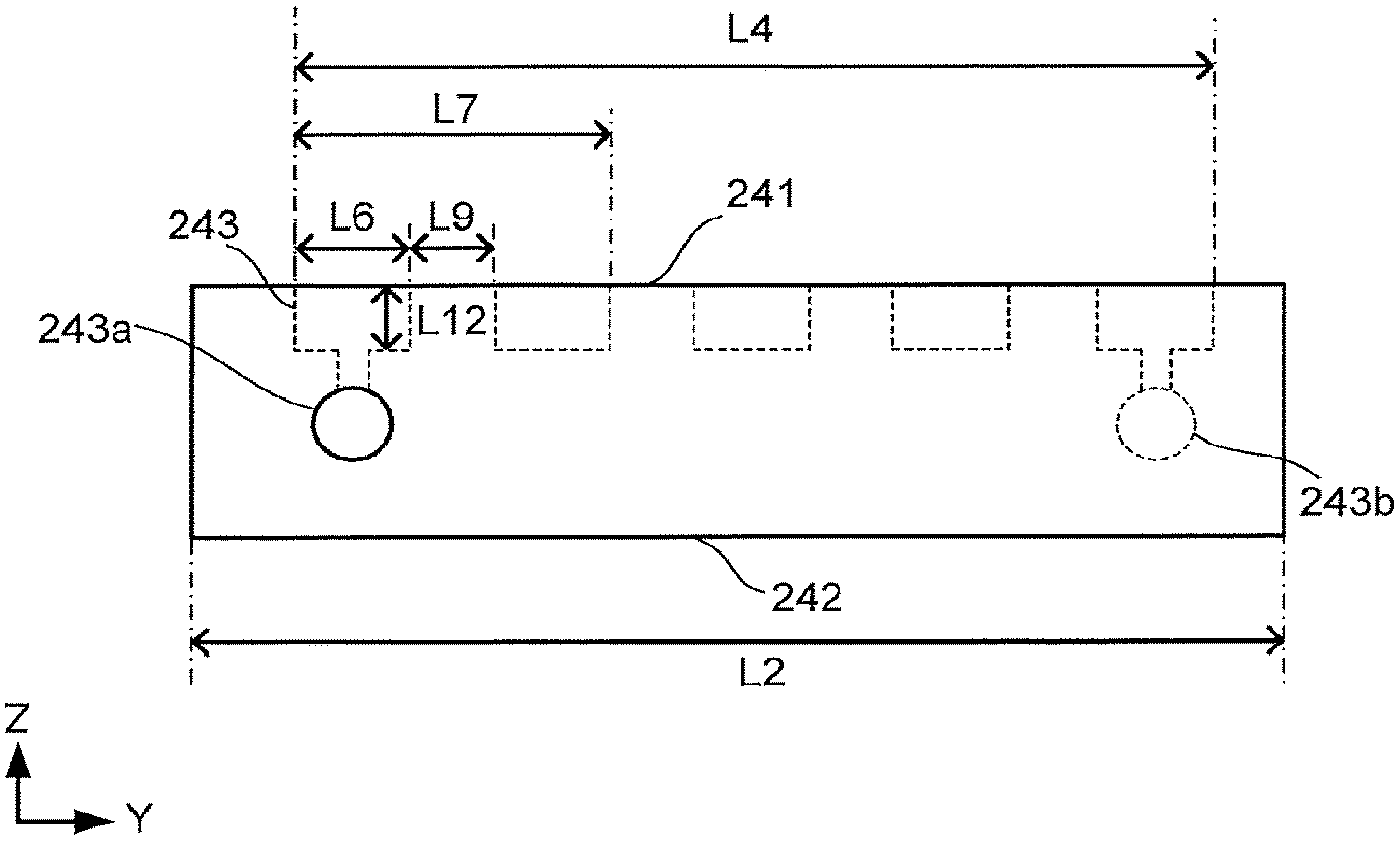

L4
L7
241
243
L6
L9
L12
243a
243b
242
L2
Z
Y

FIG.5

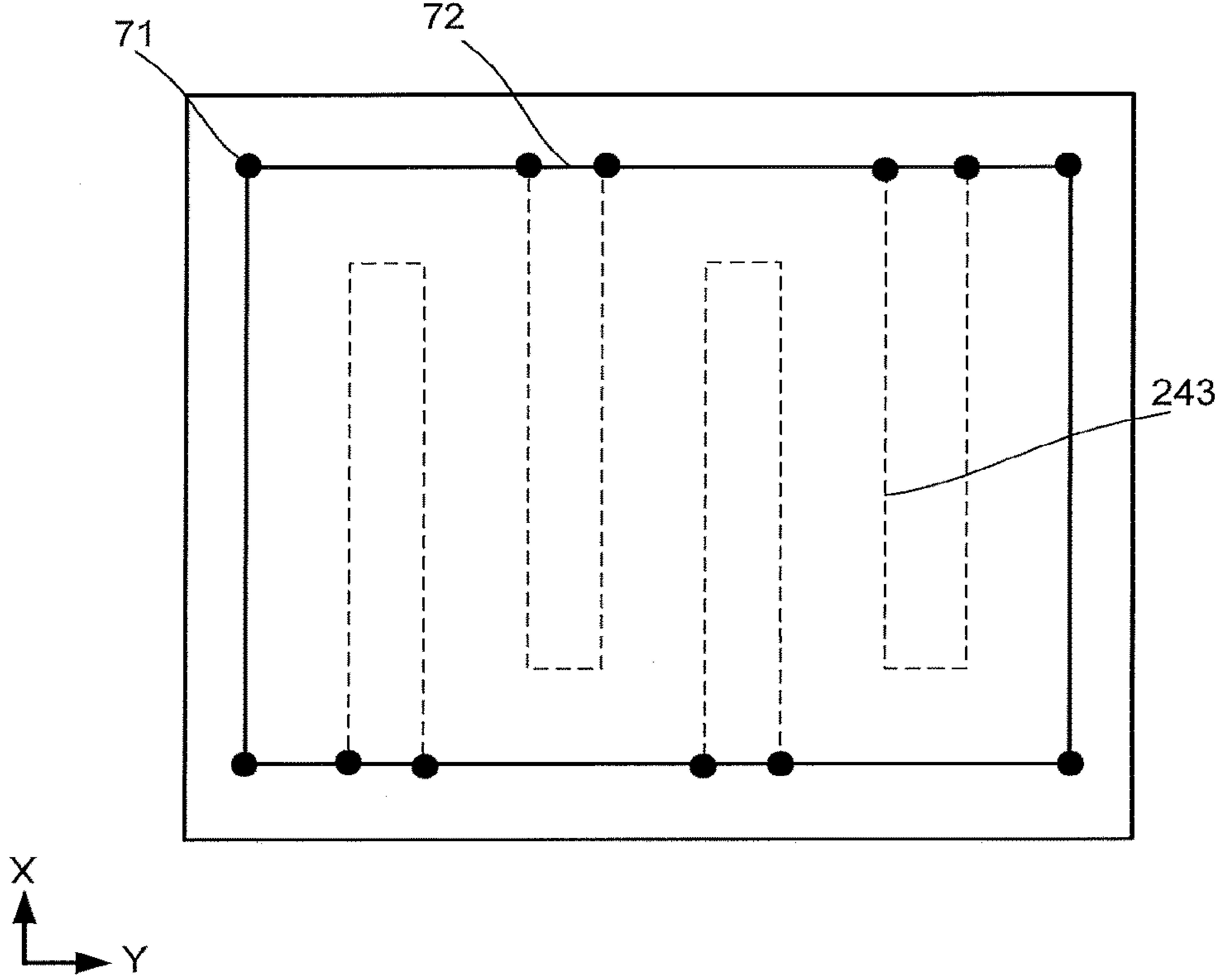


FIG.6

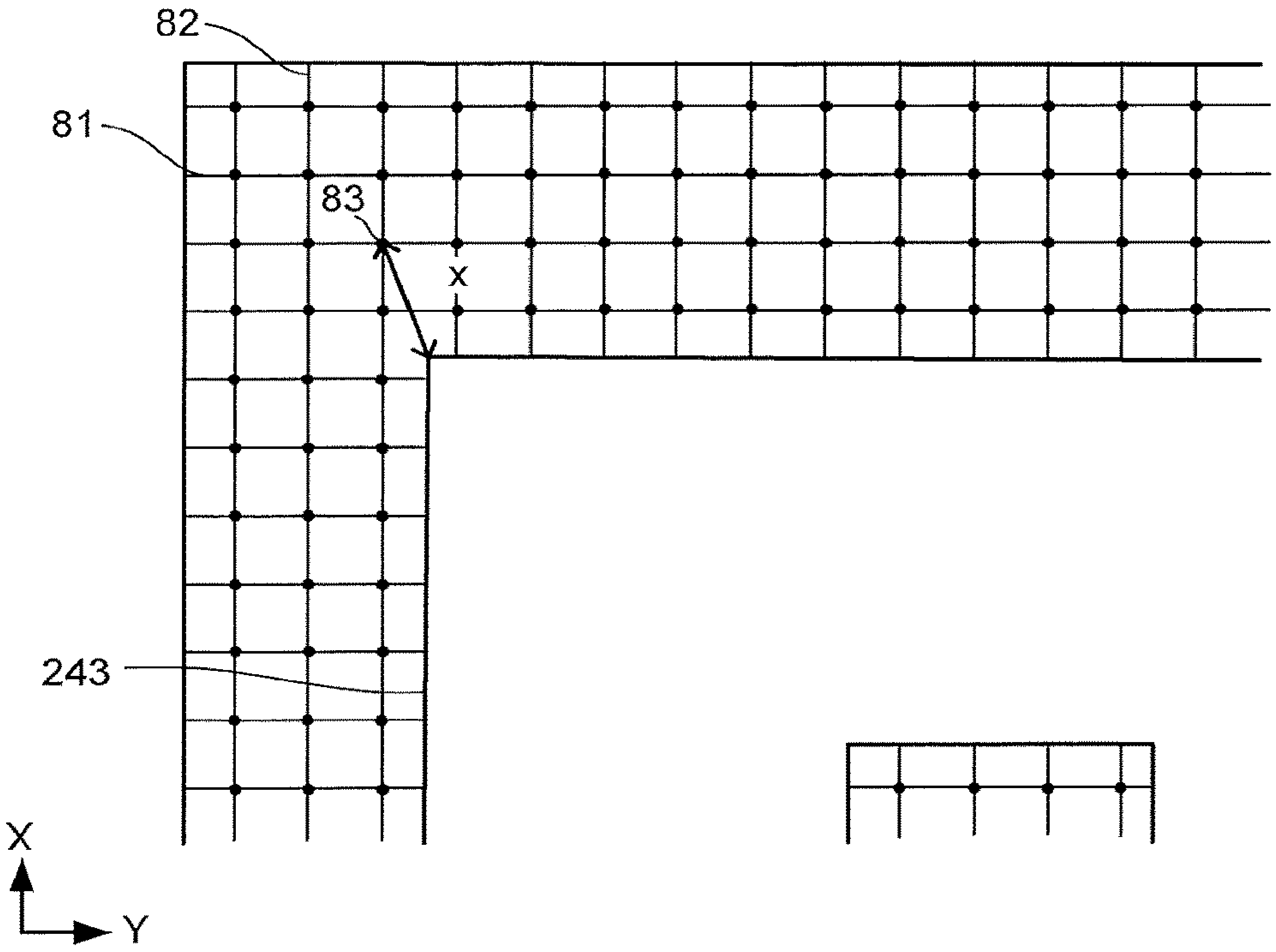


FIG.7

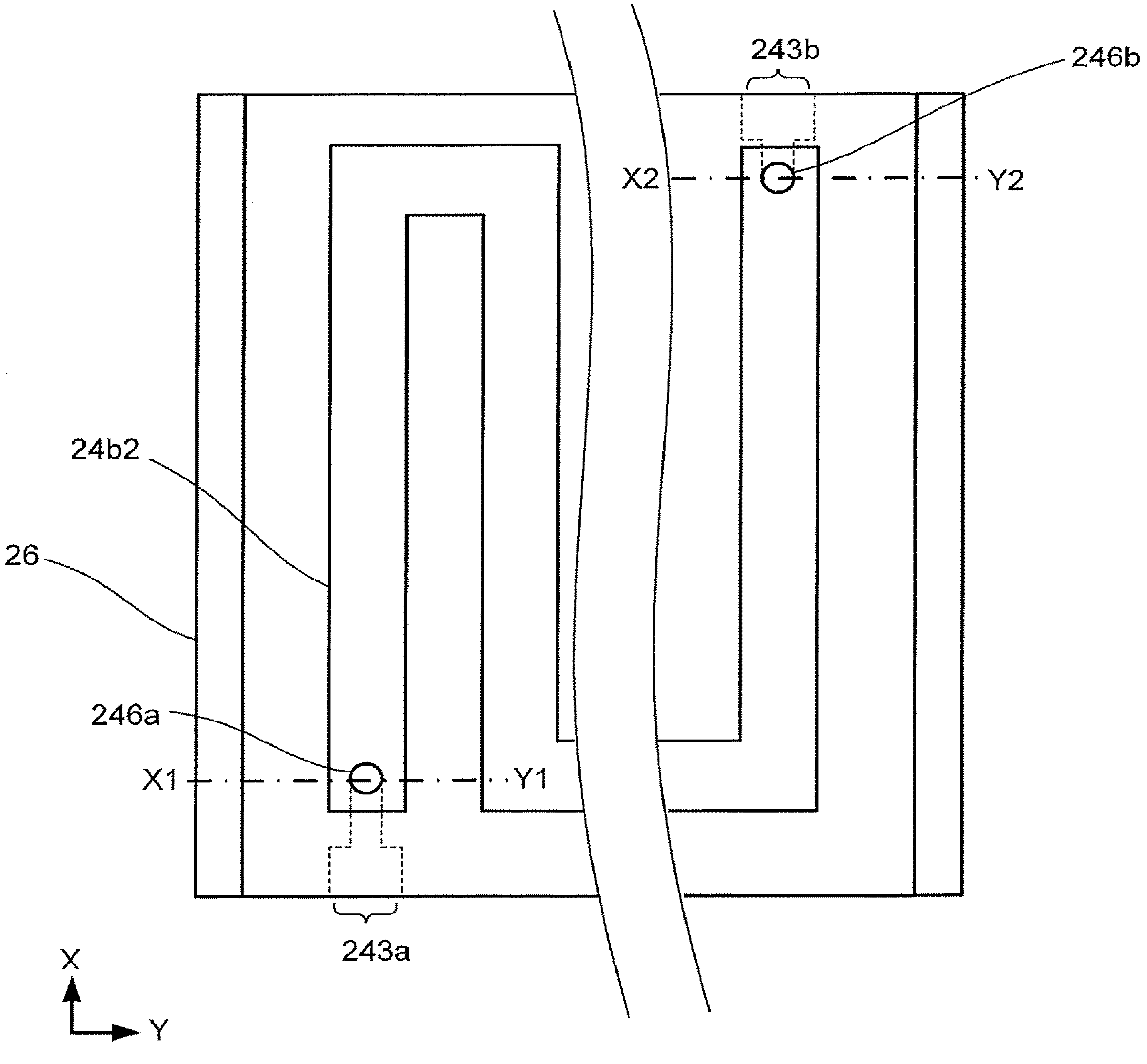


FIG.8

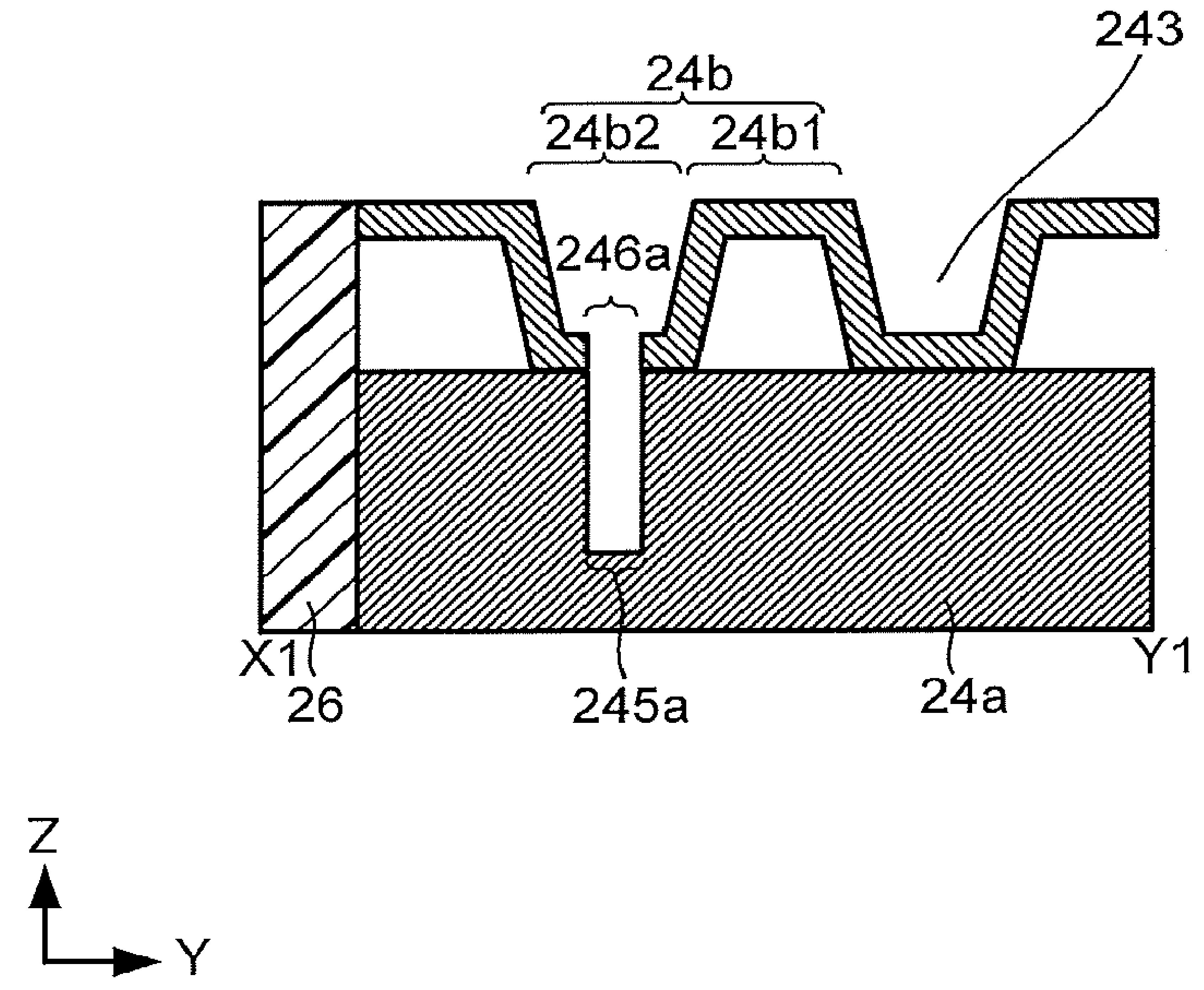

24b
24b2
24b1
243
246a
X1
26
245a
24a
Y1
Z
Y

FIG.9

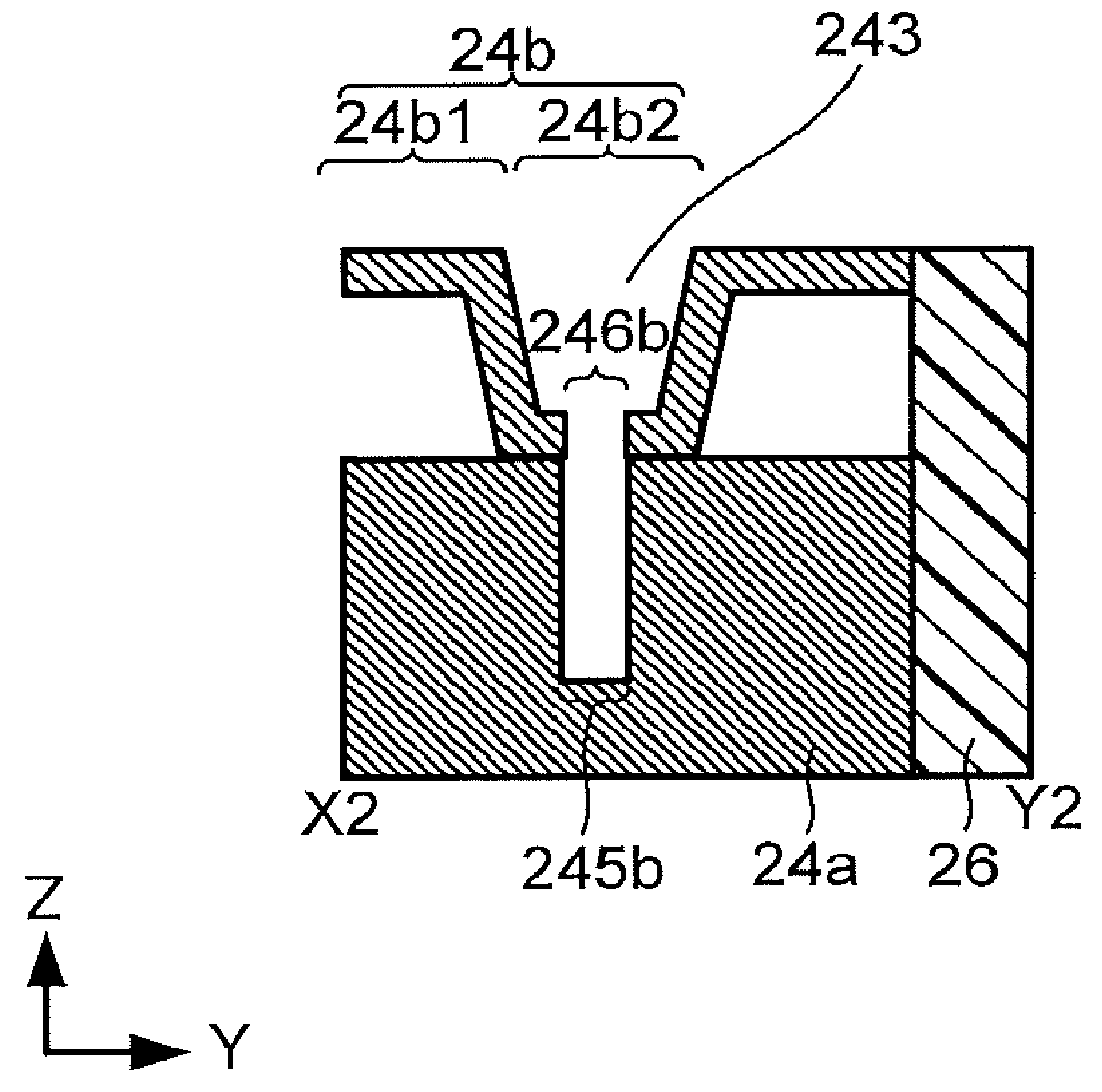

24b
24b1
24b2
243
246b
X2
245b
24a
26
Y2
Z
Y

FIG.10

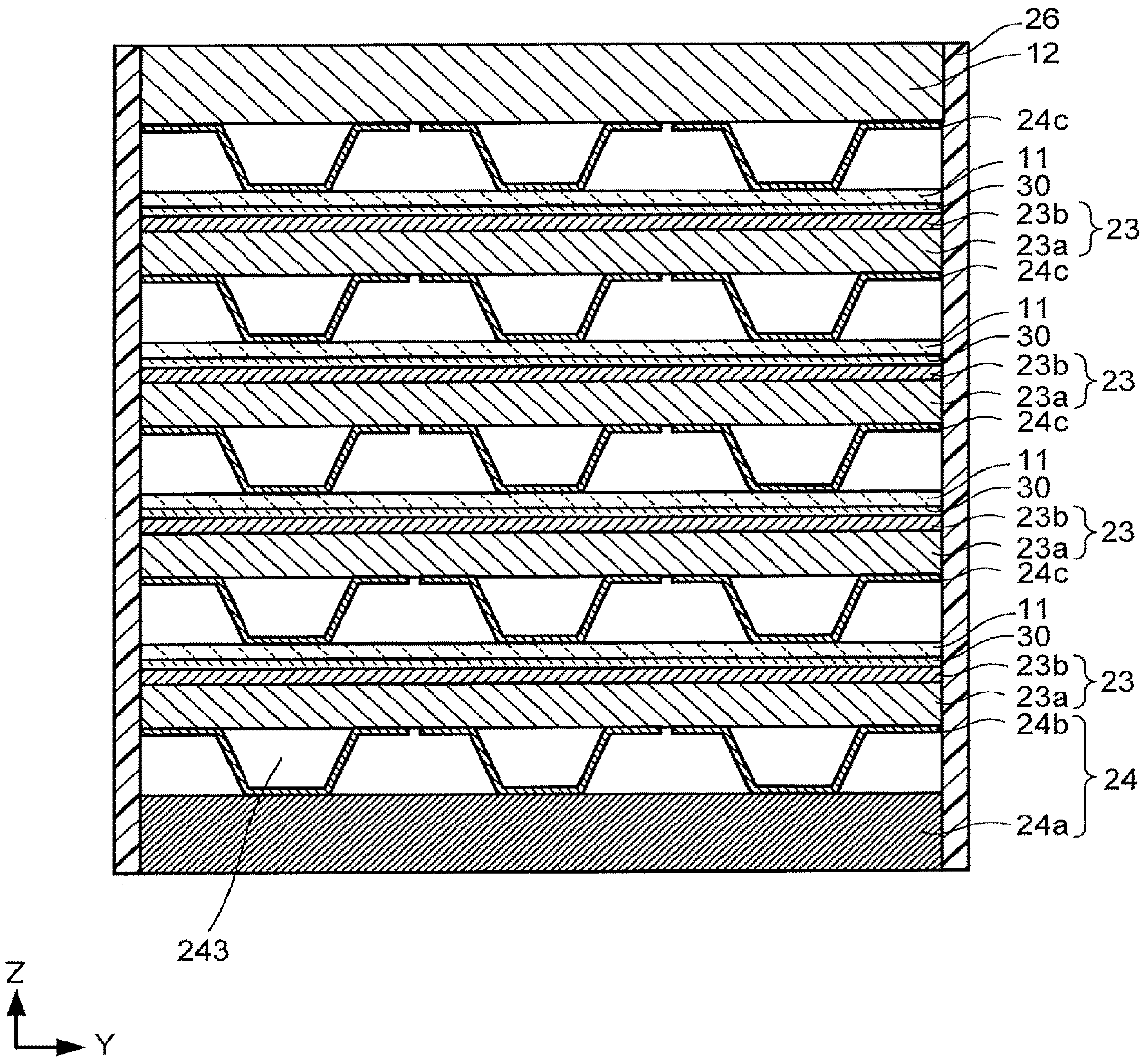

26
12
24c
11
30
23b
23a
23
24c
11
30
23b
23a
23
24c
11
30
23b
23a
23
24c
11
30
23b
23a
23
24b
24
24a
243
Z
Y

FIG.11

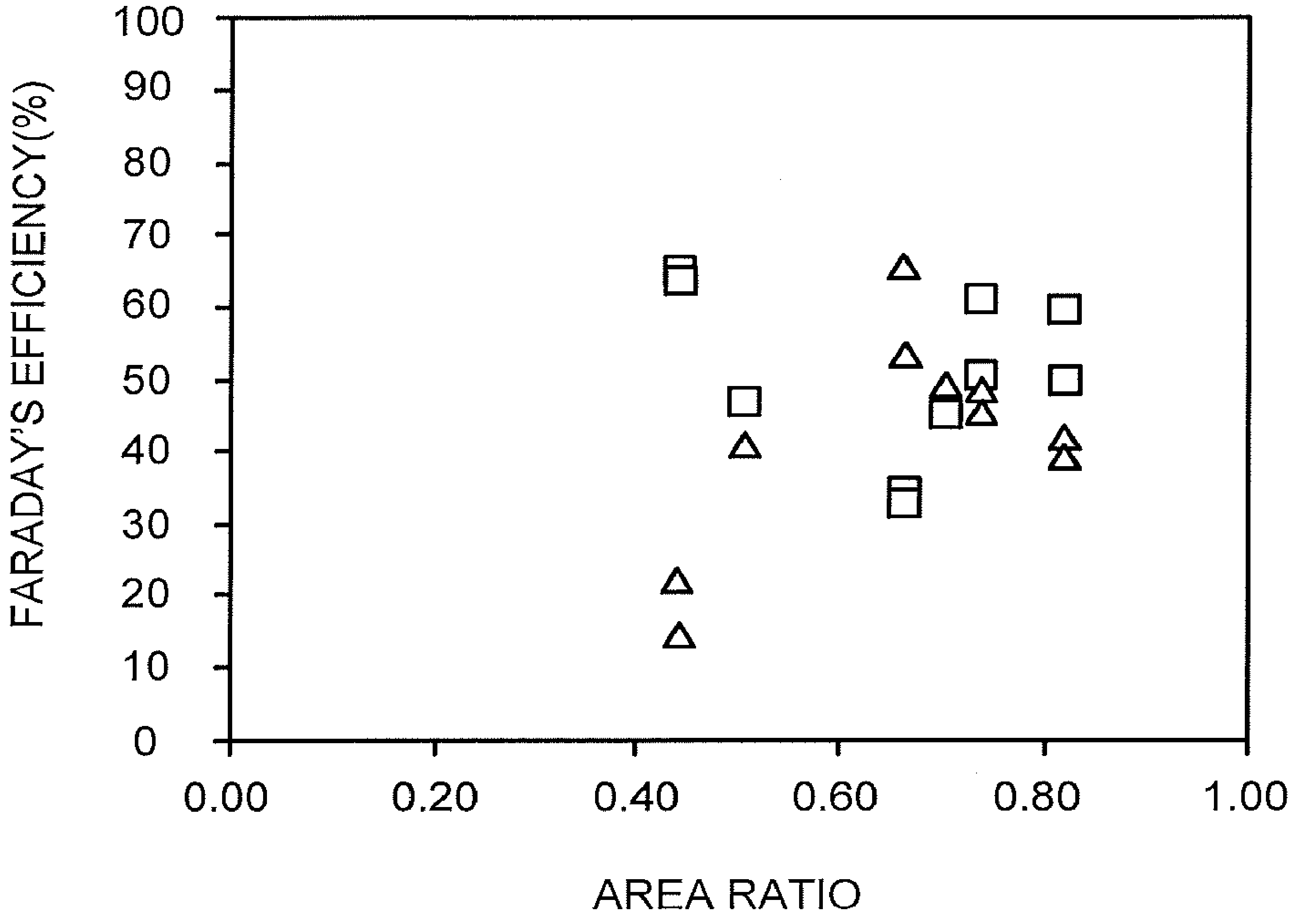

100
90
80
70
60
50
40
30
20
10
0
FARADAY'S EFFICIENCY(%)
0.00
0.20
0.40
0.60
0.80
1.00
AREA RATIO

FIG.12

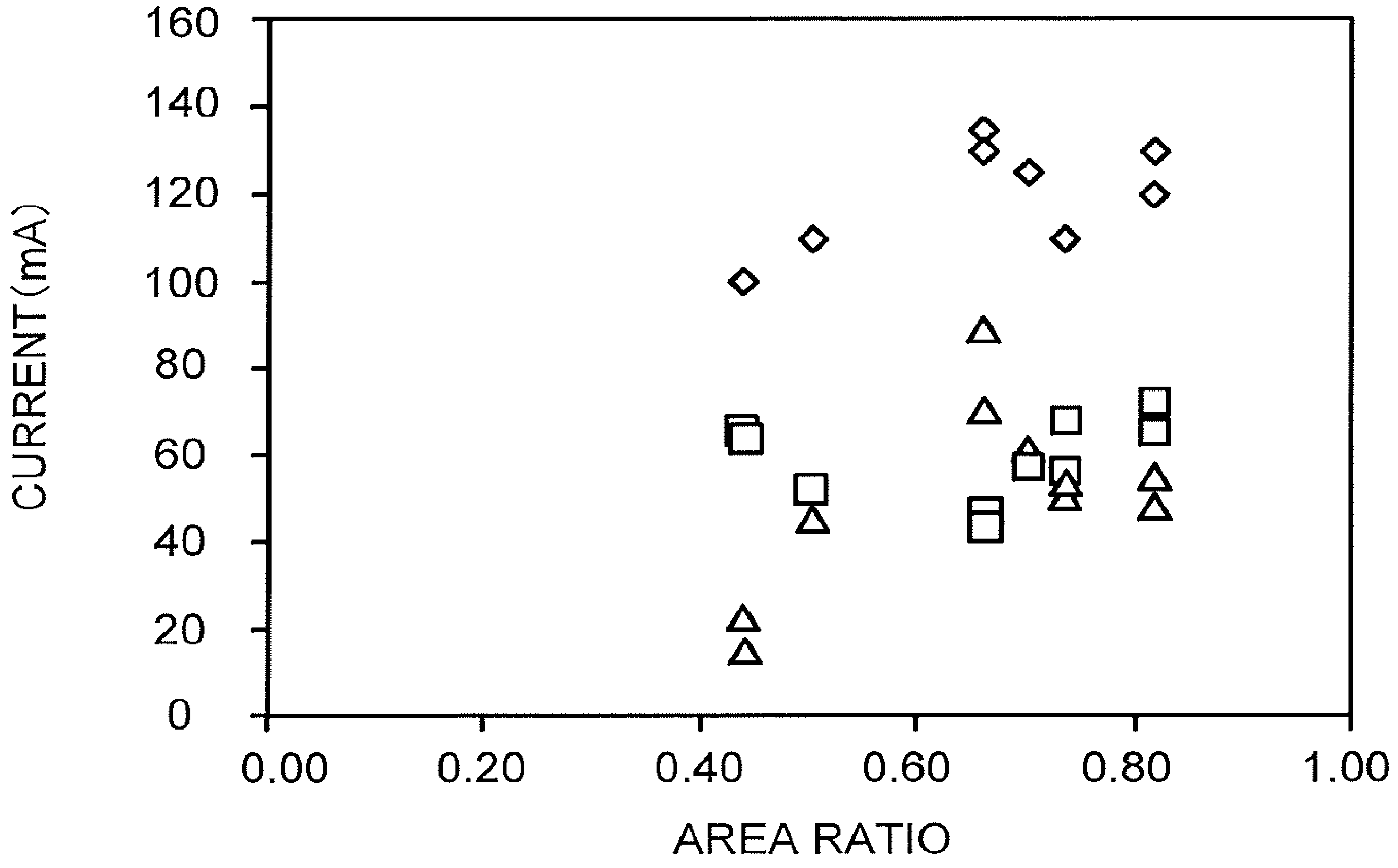

160
140
120
100
80
60
40
20
0
CURRENT(mA)
0.00
0.20
0.40
0.60
0.80
1.00
AREA RATIO

FIG.13

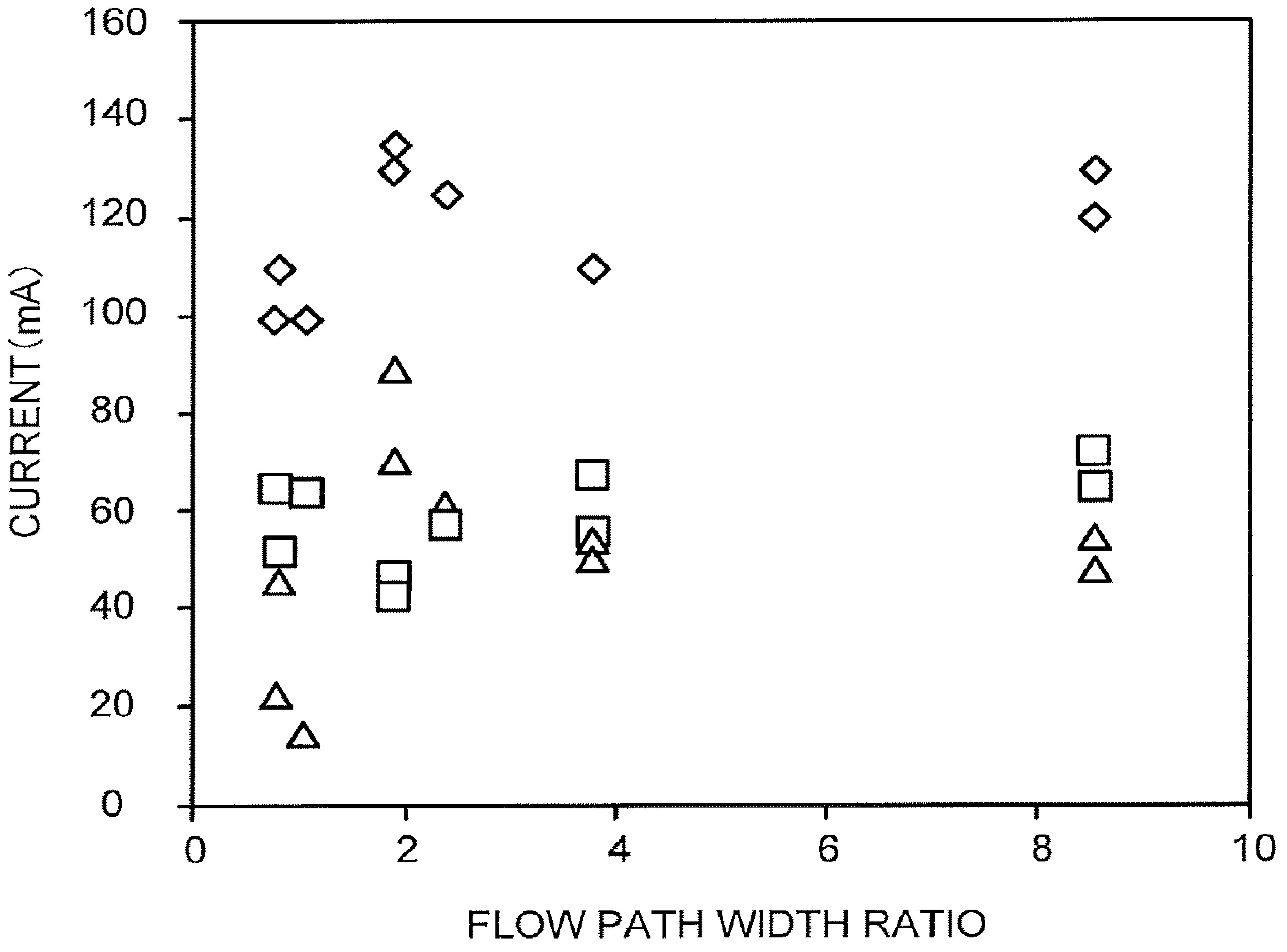

160
140
120
100
80
60
40
20
0
CURRENT (mA)
0
2
4
6
8
10
FLOW PATH WIDTH RATIO

FIG.14

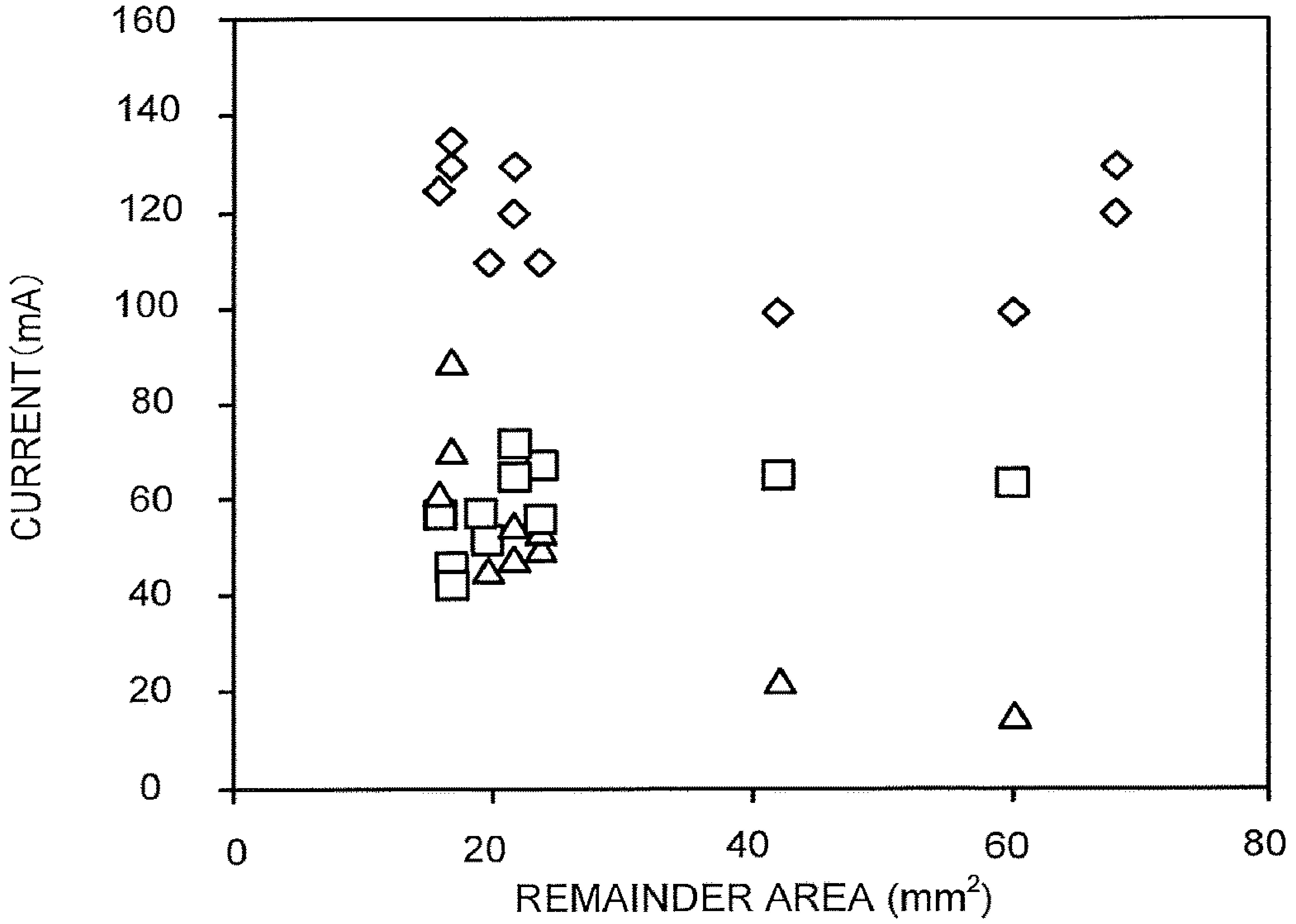

160
140
120
100
80
60
40
20
0
CURRENT (mA)
0
20
40
60
80
REMAINDER AREA (mm²)

FIG.15

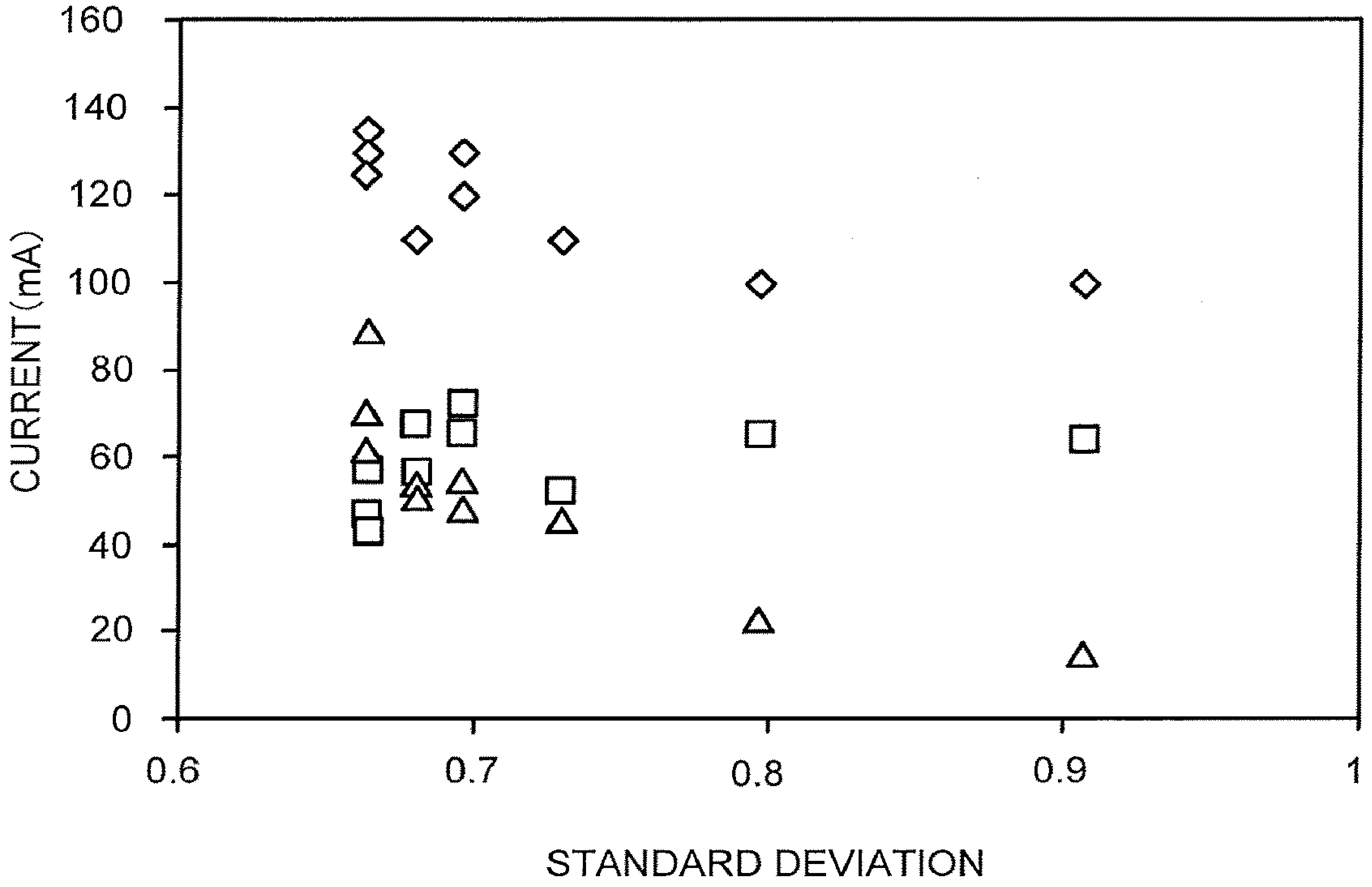
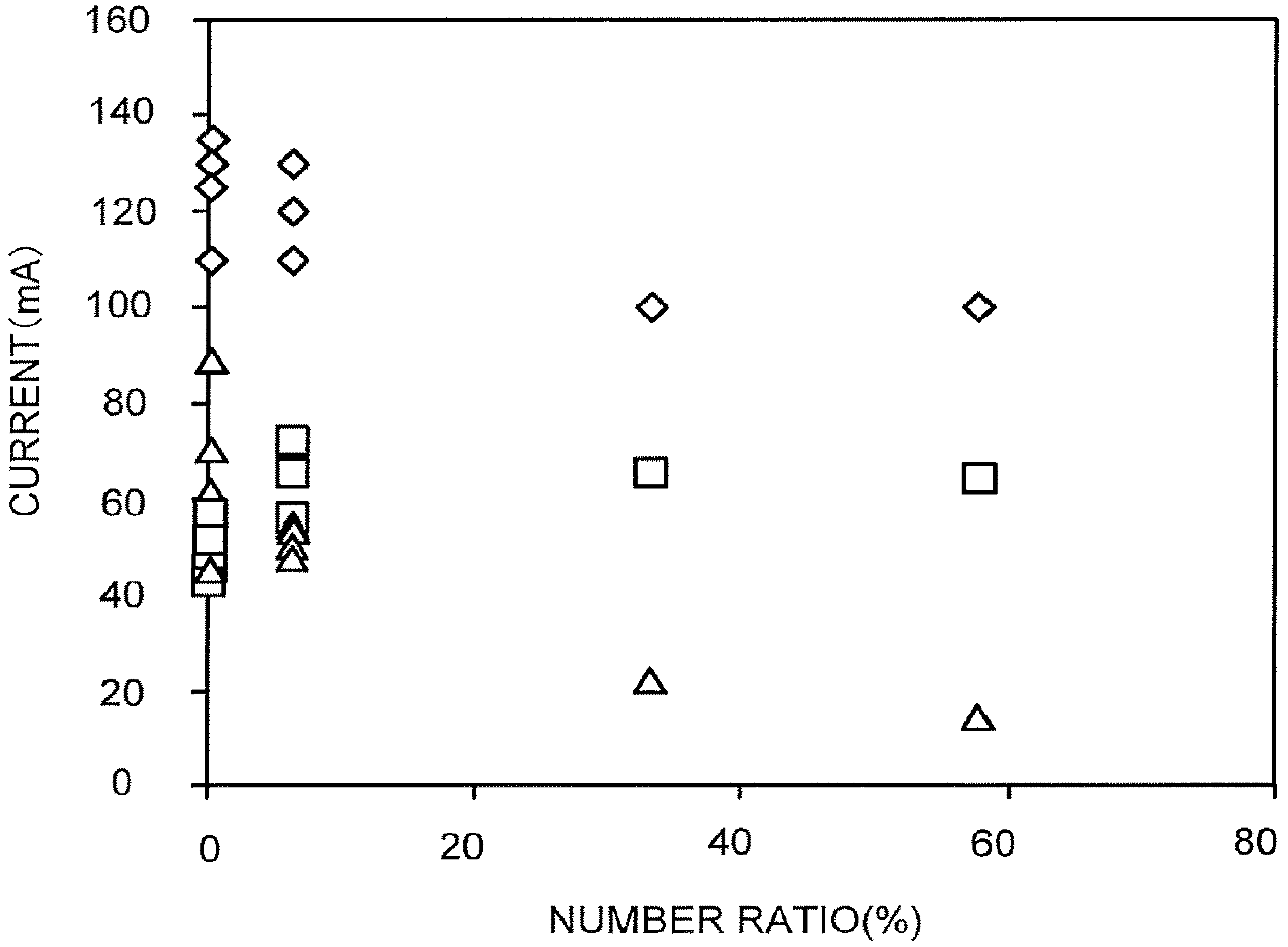

160
140
120
100
80
60
40
20
0
CURRENT(mA)
0.6
0.7
0.8
0.9
1
STANDARD DEVIATION

FIG.16


160
140
120
100
80
60
40
20
0
CURRENT(mA)
0
20
40
60
80
NUMBER RATIO(%)

ELECTROCHEMICAL REACTION DEVICE

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is based upon and claims the benefit of priority from Japanese Patent Application No. 2017-054566, filed on Mar. 21, 2017; the entire contents of which are incorporated herein by reference.

FIELD

[0002] Embodiments described herein generally relate to an electrochemical reaction device.

BACKGROUND

[0003] In recent years, from the viewpoints of both energy problems and environment problems, not only converting the renewable energy such as sunlight into the electric energy to utilize it, but also converting it into a storable and conveyable state is highly desired. In response to this demand, research and development on an artificial photosynthesis technology that produces chemical substances using the sunlight like the photosynthesis by plants are in progress. This technology also creates a possibility of storing the renewable energy as a storable fuel, and further, produces chemical substances to be industrial raw materials, and thereby, creation of value is also promising.

[0004] As a device that produces the chemical substances using the renewable energy such as the sunlight, there has been known an electrochemical reaction device that includes a cathode to reduce carbon dioxide (CO_2) from, for example, a power plant and a waste treatment plant and an anode to oxidize water (H_2O). The cathode reduces carbon dioxide to produce a carbon compound such as carbon monoxide (CO), for example. When such an electrochemical reaction device is fabricated by a cell form (to be also referred to as an electrolysis cell), fabricating the electrochemical reaction device by a form similar to a fuel cell such as a Polymer Electric Fuel Cell (PEFC), for example, is considered to be effective. However, in this case, a problem similar to a problem that the PEFC has is sometimes caused.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] FIG. **1** is a schematic view illustrating a structure example of an electrochemical reaction device.

[0006] FIG. **2** is a schematic view illustrating another structure example of the electrochemical reaction device.

[0007] FIG. **3** is a schematic top view illustrating a structure example of a part of a flow path plate.

[0008] FIG. **4** is a schematic side view illustrating a structure example of a part of the flow path plate.

[0009] FIG. **5** is a schematic view for explaining a method of calculating an area of an overlap.

[0010] FIG. **6** is a view for explaining a method of calculating a standard deviation of the shortest distance.

[0011] FIG. **7** is a schematic top view illustrating another structure example of the flow path plate.

[0012] FIG. **8** is a schematic cross-sectional view illustrating another structure example of the flow path plate.

[0013] FIG. **9** is a schematic cross-sectional view illustrating another structure example of the flow path plate.

[0014] FIG. **10** is a schematic cross-sectional view illustrating another structure example of the flow path plate.

[0015] FIG. **11** is a view illustrating the relationship between an area ratio and Faraday's efficiency.

[0016] FIG. **12** is a view illustrating the relationship between the area ratio and an overall current or a partial current.

[0017] FIG. **13** is a view illustrating the relationship between a flow path width ratio and the overall current or the partial current.

[0018] FIG. **14** is a view illustrating the relationship between an overlap remainder area and the overall current or the partial current.

[0019] FIG. **15** is a view illustrating the relationship between a standard deviation or, and the overall current or the partial current.

[0020] FIG. **16** is a view illustrating the relationship between a number ratio and the overall current or the partial current.

DETAILED DESCRIPTION

[0021] An electrochemical reaction device according to an embodiment comprises: an anode to oxidize water and thus generate oxygen; an electrolytic solution flow path facing on the anode and through which an electrolytic solution containing the water flows; a cathode including: a porous conductive layer having a first surface and a second surface; and a reduction catalyst layer having a third surface disposed on the first surface and containing a reduction catalyst to reduce carbon dioxide and thus generate a carbon compound; a separator between the anode and the cathode; a power supply connected to the anode and the cathode; and a flow path plate including: a fourth surface on the second surface; and a flow path facing on the second surface and through which the carbon dioxide flows. A ratio of an area of an overlap of the second surface and the flow path to an area of the second surface is 0.5 or more and 0.85 or less.

[0022] Hereinafter, there will be explained an embodiment with reference to the drawings. Note that the drawings are schematic and, for example, dimensions such as thickness and width of components may differ from actual dimensions of the components. Besides, in the embodiment, substantially the same components are denoted by the same reference signs and the description thereof will be omitted in some cases.

[0023] FIG. **1** and FIG. **2** are a schematic cross-sectional view illustrating a structure example of an electrochemical reaction device according to an embodiment. The electrochemical reaction device includes an anode part **10**, a cathode part **20**, a separator **30**, and a power supply **40**.

[0024] The anode part **10** can oxidize water (H_2O) to produce oxygen and hydrogen ions, or oxidize hydroxide ions (OFF) to produce water and oxygen. The anode part **10** includes an anode **11**, a flow path plate **12**, a current collector **13**, and a flow path **14**.

[0025] The anode **11** is formed by supporting an oxidation catalyst on a substrate having a porous structure such as a mesh material, a punching material, a porous body, or a metal fiber sintered body, for example. The substrate may be formed of a metal such as titanium (Ti), nickel (Ni), or iron (Fe), or a metal material such as an alloy (for example, SUS) containing at least one of these metals. The anode **11** is supported by a support or the like, for example. The support has an opening, for example, and in the opening, the anode **11** is disposed.

[0026] As the oxidation catalyst, a material that lowers activation energy for oxidizing water can be cited. In other words, a material that lowers an overvoltage when oxygen and hydrogen ions are produced through an oxidation reaction of water can be cited. For example, iridium, iron, platinum, cobalt, manganese, and so on can be cited.

[0027] Alternatively, a binary metal oxide, a ternary metal oxide, a quaternary metal oxide, or the like can be used as the oxidation catalyst. Examples of the binary metal oxide include manganese oxide (Mn—O), iridium oxide (Ir—O), nickel oxide (Ni—O), cobalt oxide (Co—O), iron oxide (Fe—O), tin oxide (Sn—O), indium oxide (In—O), ruthenium oxide (Ru—O), and so on. Examples of the ternary metal oxide include Ni—Co—O, La—Co—O, Ni—La—O, Sr—Fe—O, and so on. Examples of the quaternary metal oxide include Pb—Ru—Ir—O, La—Sr—Co—O, and so on. The oxidation catalyst is not limited to the above, and as the oxidation catalyst, a metal complex such as a Ru complex or a Fe complex can also be used. Further, a plurality of materials may be mixed.

[0028] The flow path plate **12** has a groove facing the anode **11**. The flow path plate **12** has a function as a flow path plate. As the flow path plate **12**, a material having low chemical stability and high conductivity is preferably used. Examples of such a material include metal materials such as Ti and SUS, carbon, and so on.

[0029] The current collector **13** is electrically connected to the anode **11** via the flow path plate **12**. The current collector **13** preferably contains a material having low chemical stability and high conductivity. Examples of such a material include metal materials such as Ti and SUS, carbon, and so on.

[0030] The flow path **14** contains a space between the anode **11** and the groove in the flow path plate **12**. The flow path **14** has a function as an electrolytic solution flow path for allowing a first electrolytic solution containing substances to be oxidized such as water to flow therethrough.

[0031] The cathode part **20** can reduce carbon dioxide (CO_2) to produce a carbon compound and hydrogen. The cathode part **20** includes a flow path plate **21**, a flow path **22**, a cathode **23**, a flow path plate **24** including a flow path **243**, and a current collector **25**. As illustrated in FIG. **2**, the flow path plate **21** does not need to be provided.

[0032] The flow path plate **21** has an opening having a function as the flow path **22**. The flow path **22** is provided for allowing a second electrolytic solution containing water and carbon dioxide to flow therethrough. The second electrolytic solution may contain carbon dioxide. The flow path plate **21** preferably contains a material having low chemical reactivity and no conductivity. Examples of such a material include insulating materials such as an acrylic resin, polyetheretherketone (PEEK), and a fluorocarbon resin. Changing the amount of water contained in the electrolytic solution flowing through the flow path **22** and components of the electrolytic solution makes it possible to change oxidation-reduction reactivity and change selectivity of substances to be reduced and ratios of chemical substances to be produced.

[0033] At least one of the anode **11** and the cathode **23** may have a porous structure. Examples of the material applicable to an electrode layer having the porous structure include a carbon black such as ketjen black or VULCAN XC-72, activated carbon, metal fine powder, and so on, in addition to the above-described materials. The area of an activation surface that contributes to the oxidation-reduction reaction can be made large by having the porous structure, so that it is possible to increase conversion efficiency.

[0034] As a reduction catalyst, a material that lowers activation energy for reducing hydrogen ions and carbon dioxide can be cited. In other words, a material that lowers an overvoltage when hydrogen and a carbon compound are produced through a reduction reaction of hydrogen ions and carbon dioxide can be cited. For example, a metal material or a carbon material can be used. As the metal material, for example, a metal such as platinum or nickel, or an alloy containing the metal can be used in the case of the reduction reaction of hydrogen. As the metal material, a metal such as gold, aluminum, copper, silver, platinum, palladium, or nickel, or an alloy containing the metal can be used in the case of the reduction reaction of carbon dioxide. As the carbon material, graphene, carbon nanotube (CNT), fullerene, ketjen black, or the like can be used, for example. The reduction catalyst is not limited to the above, and as the reduction catalyst, for example, a metal complex such as a Ru complex or a Re complex, or an organic molecule having an imidazole skeleton or a pyridine skeleton may be used. Further, a plurality of materials may be mixed.

[0035] An example of the carbon compound produced by the reduction reaction differs depending on the kind of the reduction catalyst. The compound produced by the reduction reaction is a carbon compound such as carbon monoxide (CO), formic acid (HCOOH), methane (CH_4), methanol (CH_3OH), ethane (C_2H_6), ethylene (C_2H_4), ethanol (C_2H_5OH), formaldehyde (HCHO), or ethylene glycol, or hydrogen, for example.

[0036] The porous structure preferably has a fine pore distribution of 5 nm or more and 100 nm or less. With the fine pore distribution, an increase in catalyst activity is enabled. Furthermore, the porous structure preferably has a plurality of fine pore distribution peaks. This can achieve all of an increase in surface area, an improvement in dispersion of ions and reactant, and high conductivity at the same time. For example, the cathode **23** may be formed by stacking a reduction catalyst layer containing particles of a metal or an alloy applicable to the above-described reduction catalyst of 100 nm or less (a particulate reduction catalyst) on a conductive layer of the above-described material having a fine pore distribution of 5 μm or more and 10 μm or less. In this case, the particle may also have the porous structure, but does not always need to have the porous structure from the conductivity or the relationship between a reaction site and material diffusion. Further, the above-described particles may be supported by another material.

[0037] The cathode **23** includes a porous conductive layer **23*a*** having a function as a gas diffusion layer, for example, and a reduction catalyst layer **23*b*** stacked on the porous conductive layer **23*a*** and containing the reduction catalyst. The cathode **23** is supported by a support, or the like, for example. The support has an opening, for example, and in the opening, the cathode **23** is disposed.

[0038] The porous conductive layer **23*a*** has a surface **23*a*1**, a surface **23*a*2** facing the flow path plate **24**, and a pore portion communicating from the surface **23*a*1** to the surface **23*a*2**. An average pore size of the pore portion is preferred to be 10 μn) or less. The porous conductive layer **23*a*** preferably has a thickness of 100 to 500 μm. In the case of the thickness being 100 μm or less, uniformity on a cell surface deteriorates, in the case of the thickness being thick, a cell thickness and a member cost increase, and further, in the case of the thickness being 500 μm or more, efficiency decreases due to an increase in gas diffusibility. The porous conductive layer **23***a* is formed of a carbon paper, a carbon cloth, or the like, for example.

[0039] The reduction catalyst layer **23***b* has a surface **23***b***1** facing the flow path **22** and a surface **23***b***2** in contact with the surface **23***a***1** of the porous conductive layer **23***a*. The reduction catalyst layer **23***b* has, for example, a porous conductive layer (mesoporous layer) having a pore size smaller than that of the porous conductive layer **23***a* and the reduction catalyst supported on a surface of the porous conductive layer. Changing water repellency and porous body degree among the porous conductive layer **23***a*, the mesoporous layer, and the reduction catalyst makes it possible to accelerate gas diffusibility and discharge of liquid components. Further, an area of the porous conductive layer **23***a* may be made larger than an area of the reduction catalyst layer **23***b*. This makes it possible to supply gas to a cell uniformly and accelerate discharge of liquid components by combining with the structure of the flow path plate **24** and the porous conductive layer **23***a*.

[0040] As the porous conductive layer, a mixture of Nafion and conductive particles such as ketjen black may be used, and as the reduction catalyst, a gold catalyst may be used. Further, formation of projections and recesses of 5 μm or less on the surface of the reduction catalyst can increase the reaction efficiency. Further, the surface of the reduction catalyst is oxidized by application of a high frequency, and then subjected to electrochemical reduction, and thereby the cathode **23** having a nanoparticle structure can be formed. Other than gold, metal such as copper, palladium, silver, zinc, tin, bismuth, or lead is preferred. Besides, the porous conductive layer may further have a stacked structure composed of layers having different pore sizes. The stacked structure having the different pore sizes makes it possible to adjust the difference in reaction due to the difference in reaction product concentration near, for example, an electrode layer, the difference in pH, or the like, by the pore sizes to improve the efficiency.

[0041] When an electrode reaction with a low current density is performed by using relatively low light irradiation energy, there is a wide range of options in catalyst material. Accordingly, for example, it is easy to perform a reaction by using a ubiquitous metal or the like, and it is also relatively easy to obtain selectivity of the reaction. When the power supply **40** formed of a photoelectric conversion body is electrically connected to at least one of the anode **11** and the cathode **23** by a wire or the like, an electrode area generally becomes small for the reason of miniaturizing an electrolytic solution tank to achieve space saving, cost reduction, or the like, and the reaction is performed with a high current density in some cases. In this case, a noble metal is preferably used as the catalyst.

[0042] The electrochemical reaction device according to this embodiment is a simplified system, in which the anode **11** and the cathode **23** are integrated to reduce the number of parts. Accordingly, for example, manufacture, installation, and maintainability improve.

[0043] FIG. **3** is a schematic top view illustrating a structure example of a part of the flow path plate **24**. FIG. **3** illustrates an X-Y plane of the flow path plate **24** including an X axis and a Y axis perpendicular to the X axis. FIG. **4** is a schematic side view illustrating a structure example of a part of the flow path plate **24**. FIG. **4** illustrates a Y-Z plane of the flow path plate **24** including the Y axis and a Z axis perpendicular to the Y axis and the X axis. In FIG. **3** and FIG. **4**, only an overlap of the flow path plate **24** and the surface **23***b***2** or the surface **23***a***2** is schematically illustrated.

[0044] The flow path plate **24** includes a surface **241**, a surface **242**, and the flow path **243**. The surface **241** is in contact with the porous conductive layer **23***a*. The surface **242** faces the surface **241**, and is in contact with the current collector **25**. The flow path plate **24** illustrated in FIG. **3** and FIG. **4** has a rectangular parallelepiped shape, but is not limited to this.

[0045] The flow path **243** faces the surface **23***a***2** of the porous conductive layer **23***a*. The flow path **243** communicates with an inflow port **243***a* and an outflow port **243***b*. The inflow port **243***a* is provided in order to allow carbon dioxide to flow into the flow path **243** from the outside of the flow path plate **24** (outside of the cathode part **20**). At least a part of the above-described carbon dioxide is gaseous. The outflow port **243***b* is provided in order to allow the carbon dioxide to flow out to the outside of the flow path plate **24** (outside of the cathode part **20**) from the flow path **243** and allow a reaction product produced by the reduction reaction to flow out to the outside of the flow path plate **24**.

[0046] The flow path **243** illustrated in FIG. **3** extends in a serpentine shape along the surface **241**. The flow path **243** is not limited to this, and may extend in a comb-teeth shape or a spiral shape along the surface **241**. The flow path **243** contains spaces formed by grooves and openings provided in the flow path plate **24**, for example.

[0047] The flow path **243** has a plurality of regions **243***c* and a plurality of regions **243***d*. One of the regions **243***c* extends along an X-axis direction of the surface **241**. One of the regions **243***d* extends so as to turn back from one of the regions **243***c* along the surface **241**. Another of the regions **243***c* extends along the X-axis direction of the surface **241** from the region **243***d*.

[0048] A length in the X-axis direction of an overlap of the surface **241** and the surface **23***a***2** or the surface **23***b***2** is defined as L**1**. A length in a Y-axis direction of the overlap of the surface **241** and the surface **23***a***2** or the surface **23***b***2** is defined as L**2**. A length in the X-axis direction of an overlap of the surface **23***a***2** or the surface **23***b***2** and the flow path **243** is defined as L**3**. A length in the Y-axis direction of the overlap of the surface **23***a***2** or the surface **23***b***2** and the flow path **243** is defined as L**4**. A length of the region **243***c* is defined as L**5**. An average width of the region **243***c* is defined as L**6**. A length of the region **243***d* is defined as L**7**. An average width of the region **243***d* is defined as L**8**. An average width between one of the regions **243***c* and another of the regions **243***c* is defined as L**9**. The shortest distance between an end portion in the X-axis direction of the overlap of the surface **241** and the surface **23***a***2** or the surface **23***b***2** and the flow path **243** is defined as L**10**. The shortest distance between an end portion in the Y-axis direction of the overlap of the surface **241** and the surface **23***a***2** or the surface **23***b***2** and the flow path **243** is defined as L**11**. A depth in a Z-axis direction of the flow path **243** is defined as L**12**.

[0049] A ratio of an area of an overlap of the surface **23***a***2** and the flow path **243** to an area of the surface **23***a***3** is preferred to be 0.5 or more and 0.85 or less. Further, a ratio of an area of an overlap of the surface **23***b***2** and the flow path **243** to an area of the surface **23***b***2** is preferred to be 0.5 or more and 0.85 or less.

[0050] As the amount of gas changes due to the reaction between the vicinity of the inflow port **243***a* and the vicinity of the outflow port **243***b*, a flow speed changes in some cases. In contrast to this, for example, the width of the flow path **243** is tapered toward the outflow port **243***b*, or the number of branches of the flow path **243** in parallel connection is changed, thereby making it possible to increase uniformity of the entire reduction reaction of the cathode **23**. When a value obtained by dividing an integrated value of the width of the flow path **243** with respect to the entire length of the flow path **243** by the above-described entire length is used as a mean value and a value obtained by dividing an integrated value of, with respect to the entire length of a region between one of the regions **243***c* and another of the regions **243***c*, a width of the above-described region by the above-described entire length is used as a mean value, the width of the above-described region is preferably smaller than the width of the flow path **243**. This enables efficient supply of a carbon dioxide gas to the porous conductive layer **23***a*. However, when the above-described width is small extremely, the gas or the like becomes likely to be supplied through the above-described region rather than the flow path **243**. A ratio of the average width of the region **243***c* of the flow path **243** (L**6**) to the average width between one of the regions **243***c* and another of the regions **243***c* (L**9**) is preferred to be 1.5 or more and 5 or less.

[0051] Although the flow path **243** can be formed variously, the carbon dioxide gas is supplied in an overlap of the flow path **243** and the porous conductive layer **23***a*. By changing the flow rate of the carbon dioxide gas and the flow path width, the flow speed is changed to adjust pressure or the like, resulting in an increase in partial pressure of the carbon dioxide. Further, discharges of the produced water and the water that has migrated from the oxidation side are also accelerated by circulation of the carbon dioxide gas. In the meantime, the mobility of the produced water and the water that has migrated from the oxidation side between the regions **243***c* is inferior to that in the region facing the flow path **243**, and moisture amounts in the porous conductive layer **23***a* and of the reduction catalyst layer **23***b* are higher. From this viewpoint, when the area between the regions **243***c* is large, hydrogen generation is large and reduction performance of the carbon dioxide decreases. Further, when the width between the regions **243***c* is wide, discharge of water to the flow path **243** from a center portion between the regions **243***c* and a supply amount of the carbon dioxide to between the regions **243***c* from the flow path **243** decrease. Therefore, the hydrogen generation increases and cell performance decreases. Further, there are no adjacent flow paths in a region outside a region, of the reduction catalyst layer **23***b* and the porous conductive layer **23***a*, surrounding the outer periphery of the flow path **243**, and therefore, when the width of the periphery between the regions **243***c* is large, an increase in production rate of the hydrogen results in a significant impact.

[0052] It is impossible to say that the region between one of the regions **243***c* and another of the regions **243***c* only needs to be narrow, and there is sometimes a case that the difference in pressure loss between the porous conductive layer **23***a* and the flow path **243** prevents the gas from flowing through the flow path **243** to make the gas flow through the above-described region easily. In this case, the surface uniformity of the reaction is impaired and the reaction efficiency of the electrochemical reaction device decreases. Furthermore, due to the small area of the above-described region, a contact area between the porous conductive layer **23***a* and the flow path plate **24** decreases, resulting in that a contact resistance increases and the reaction efficiency of the electrochemical reaction device decreases.

[0053] The area of the surface **23***a***2** is made larger than the area of the surface **23***b***2**, thereby making it possible to facilitate uniform adjustment of the amounts of the gas and the moisture to the porous conductive layer **23***a*, so that it is possible to improve the reaction efficiency. However, when the area of the surface **23***a***2** is much larger than the area of the surface **23***b***2**, the cell area becomes large, resulting in a decrease in the efficiency due to effects of cost, productivity, heat release, and the like.

[0054] If the surface **23***a***2** is divided into a polygonal portion and a remainder portion, the polygonal portion is formed by connecting vertexes of the overlap of the surface **23***a***2** and the flow path **243**, each of interior angles of the overlap thereof corresponding to the vertexes is less than 180 degrees, and a ratio of an area of the remainder portion to the area of the surface **23***a***2** is preferred to be ⅙ or less. FIG. **5** is a schematic view for explaining a method of calculating the area of an overlap. FIG. **5** illustrates vertexes **71**, out of vertexes of the overlap, each having an interior angle of less than 180 degrees, and a polygon **72** formed by connecting the vertexes **71**. Furthermore, a ratio of an area of the remainder of the surface **23***b***2** from which the overlap and the polygon **72** are removed to the area of the surface **23***b***2** is preferred to be ⅙ or less.

[0055] As a distance to the overlap of the surface **23***a***2** or the surface **23***b***2** and the flow path **243** is farther and farther from respective points of the overlap of the surface **23***a***2** or the surface **23***b***2** and the surface **241**, the hydrogen rather than the carbon compound is produced by the reduction reaction dominantly. Further, when the overlap of the surface **23***a***2** or the surface **23***b***2** and the surface **241** includes a lot of portions far from the overlap of the surface **23***a***2** or the surface **23***b***2** and the flow path **243**, the reduction performance of the carbon dioxide decreases. Thus, reducing a standard deviation of the shortest distances between respective points of the overlap of the surface **23***a***2** or the surface **23***b***2** and the surface **241** and the overlap of the surface **23***a***2** or the surface **23***b***2** and the flow path **243** enables an improvement in the reduction performance of the carbon dioxide.

[0056] The standard deviation of the shortest distance is preferred to be 0.8 or less. FIG. **6** is a view for explaining a method of calculating the standard deviation of the shortest distance. FIG. **6** illustrates: a plurality of parting lines **81** dividing the remainder of the overlap of the surface **23***a***2** or the surface **23***b***2** and the surface **241** from which the overlap of the surface **23***a***2** or the surface **23***b***2** and the flow path **243** is removed along the X-axis direction by 0.1 mm each; a plurality of parting lines **82** dividing the above-described remainder along the Y-axis direction by 0.1 mm each; a plurality of intersection points **83** of the parting lines **81** and the parting lines **82**; and the shortest distance x between the intersection point **83** and the above-described overlap.

[0057] A standard deviation a is defined by calculating the square of the shortest distance x between the intersection point **83** and the above-described overlap at each intersection point **83** and calculating a square root of a value obtained by dividing the sum of the calculated squares of the shortest distances x by an intersection point number n. That is, the standard deviation a is expressed by the following expression (A).

[Mathematical expression 1]

$$\textcircled{?} = \sqrt{\frac{1}{\textcircled{?}}\textcircled{?}\, x^2} \tag{A}$$

$\textcircled{?}$ indicates text missing or illegible when filed

[0058] In the remainder of the overlap, the number of intersection points, at which the shortest distance x is 0.5 mm or more, is preferred to be 30% or less of a number n of all the intersection points **83**.

[0059] The depth of the flow path **243** in the Z-axis direction is preferably shallow from the viewpoints of supplying the carbon dioxide to the porous conductive layer **23***a*, discharging the liquid, and performing the reaction uniformly on the cell surface. However, the flow path being narrow increases the pressure loss of the flow path, thereby causing an energy loss of the gas supply and flowing through not the flow path but the gas diffusion layer, and thereby the uniform reaction on the cell surface is prevented. Thus, an extremely narrow flow path is not preferred. The depth of the flow path **243** preferably falls within a range of 0.3 to 2 mm. When the depth is less than 0.3 mm, the porous conductive layer **23***a* digs into the flow path **243**. Therefore, the actual width of the flow path becomes narrower, so that narrowing the flow path width and setting the depth to about 0.5 mm are preferred. When the flow path **243** has a too large depth, the gas supply deteriorates due to an effect of diffusion, so that the depth is preferred to be at least 2 mm or less.

[0060] As the first electrolytic solution and the second electrolytic solution, an aqueous solution containing, for example, $LiHCO_3$, $NaHCO_3$, $KHCO_3$, $CsHCO_3$, phosphoric acid, boric acid, or the like may be used. Further, as the first electrolytic solution and the second electrolytic solution, an aqueous solution containing, for example, an optional electrolyte can be used. Examples of the aqueous solution containing the electrolyte include aqueous solutions containing phosphoric acid ions (PO_4^{2-}), boric acid ions (BO_3^{3-}), sodium ions (Na^+), potassium ions (K^+), calcium ions (Ca^{2+}), lithium ions (Li^+), cesium ions (Cs^+), magnesium ions (Mg^{2+}), chloride ions (Cl^-), hydrogen carbonate ions (HCO_3^-), carbonate ions (CO_3^-), or the like. The first electrolytic solution and the second electrolytic solution may contain substances different from each other.

[0061] As the above-described electrolytic solutions, for example, an ionic liquid that is made of a salt of cations such as imidazolium ions or pyridinium ions and anions such as BF_4^- or PF_6^- and that is in a liquid state in a wide temperature range, or an aqueous solution thereof can be used. Other examples of the electrolytic solution include amine solutions of ethanolamine, imidazole, pyridine, and so on, and aqueous solutions thereof. Examples of the amine include primary amine, secondary amine, tertiary amine, and so on. These electrolytic solutions may have high ion conductivity, have a property of absorbing carbon dioxide, and have characteristics of decreasing reduction energy.

[0062] Examples of the primary amine include methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, and so on. A hydrocarbon of the amine may be substituted by alcohol or halogen. Examples of the amine whose hydrocarbon is substituted include methanolamine, ethanolamine, chloromethyl amine, and so on. Further, an unsaturated bond may exist. The same applies to hydrocarbons of the secondary amine and the tertiary amine.

[0063] Examples of the secondary amine include dimethylamine, diethylamine, dipropylamine, dibutylamine, dipentylamine, dihexylamine, dimethanolamine, diethanolamine, dipropanolamine, and so on. The substituted hydrocarbons may be different. The same applies to the tertiary amine. Examples of amine in which substituted hydrocarbons are different include methylethylamine, methylpropylamine, and so on.

[0064] Examples of the tertiary amine include trimethylamine, triethylamine, tripropylamine, tributylamine, trihexylamine, trimethanolamine, triethanolamine, tripropanolamine, tributanolamine, triexanolamine, methyl diethylamine, methyldipropylamine, and so on.

[0065] Examples of the cations of the ionic liquid include 1-ethyl-3-methylimidazolium ions, 1-methyl-3-propylimidazolium ions, 1-butyl-3-methylimidazole ions, 1-methyl-3-pentylimidazolium ions, 1-hexyl-3-methylimidazolium ions, and so on.

[0066] A second place of the imidazolium ion may be substituted. Examples of the cation having the imidazolium ion in which the second place is substituted include 1-ethyl-2,3-dimethylimidazolium ions, 1-2-dimethyl-3-propylimidazolium ions, 1-butyl-2,3-dimethylimidazolium ions, 1,2-dimethyl-3-pentylimidazolium ions, 1-hexyl-2,3-dimethylimidazolium ions, and so on.

[0067] Examples of the pyridinium ion include methylpyridinium, ethylpyridinium, propylpyridinium, butylpyridinium, pentylpyridinium, hexylpyridinium, and so on. In both of the imidazolium ion and the pyridinium ion, an alkyl group may be substituted, or an unsaturated bond may exist.

[0068] Examples of the anion include fluoride ions, chloride ions, bromide ions, iodide ions, BF_4^-, PF_6^-, CF_3COO^-, $CF_3SO_3^-$, NO_3^-, SCN^-, $(CF_3SO_2)_3C^-$, bis(trifluoromethoxysulfonyl)imide, bis(perfluoroethylsulfonyl)imide, and so on. A dipolar ion in which the cation and the anion of the ionic liquid are coupled by hydrocarbons may be used. A buffer solution such as a potassium phosphate solution may be supplied to the flow paths.

[0069] The flow path plate **24** is preferred to be a metal plate containing a material having low chemical reactivity and high conductivity. As such a material, metal plates of Ti, SUS, and so on can be cited.

[0070] The current collector **25** is in contact with the surface **242** of the flow path plate **24**. The current collector **25** preferably contains a material having low chemical reactivity and high conductivity. As such a material, metal materials such as Ti and SUS, carbon, and so on can be cited.

[0071] The separator **30** is formed of an ion exchange membrane or the like that enables ions to migrate between the anode part **10** and the cathode part **20** and separation between the anode **11** and the cathode **23**. The ion exchange membrane allows specific ions to pass therethrough. Examples of the ion exchange membrane include Neosepta (registered trademark) manufactured by ASTOM Corporation, Selemion (registered trademark) and Aciplex (registered trademark) manufactured by Asahi Glass Co. Ltd., Fumasep (registered trademark) and fumapem (registered trademark) manufactured by Fumatech GmbH, Nafion (registered trademark), which is a fluorocarbon resin produced through polymerization of sulfonated tetrafluoroethylene, manufactured by Du Pont, lewabrane (registered trademark) manufactured by LANXESS, IONSEP (registered trademark) manufactured by IONTECH, Mustang (registered trademark) manufactured by Pall Corporation, ralex (registered trademark) manufactured by mega a.s., Gore-Tex (registered trademark) manufactured by W. L. Gore & Associates, and so on. Further, the ion exchange membrane may be formed of a film having a hydrocarbon basic skeleton or for anion exchange, may be formed of a film having an amine group.

[0072] When a solid electrolyte membrane is used as the electrolyte, the aforementioned Nafion, Selemion, or the like is used. Further, the electrolyte is not limited to the solid electrolyte membrane, and may be an electrolytic solution of alkali or the like. At this time, a narrow interval between the anode **11** and the cathode **23** is preferred because an electrical resistance becomes low, and further a uniform interval between the anode **11** and the cathode **23** is preferred because an electrical resistance to an electrode surface becomes uniform and the reaction efficiency becomes high. Therefore, a porous nonconductive membrane is preferably provided between the anode **11** and the cathode **23**. This enables migration of the electrolyte through the porous body, the interval between the anode **11** and the cathode **23** is uniformized between several μm and several hundred μm, and separation of gas components present in the anode **11** and cathode **23** is enabled. As such a membrane, a water-repellent porous polymer such as Teflon, or a porous substance subjected to a water-repellent treatment such as Teflon is used.

[0073] When the ion exchange membrane is a proton exchange membrane, for example, migration of the hydrogen ions is enabled. Use of the ion exchange membrane being a solid polymer membrane such as Nafion can increase the migration efficiency of the ions. The ion exchange membrane is not necessarily provided, and a salt bridge such as agar may be provided in place of the ion exchange membrane, or a porous body thin film may be used.

[0074] The power supply **40** is electrically connected to the anode **11** and the cathode **23**. With use of the electric energy supplied from the power supply **40**, the reduction reaction by the cathode **23** and the oxidation reaction by the anode **11** are performed. For example, a wire may connect the power supply **40** and the anode **11** and connect the power supply **40** and the cathode **23**. The power supply **40** includes a photoelectric conversion element, a system power supply, a power supply device such as a storage battery, or a conversion unit that converts renewable energy such as wind power, water power, geothermal power, or tidal power into electric energy. For example, the photoelectric conversion element has a function of separating charges using energy of irradiating light such as sunlight. Examples of the photoelectric conversion element include a pin-junction solar cell, a pn-junction solar cell, an amorphous silicon solar cell, a multijunction solar cell, a single crystal silicon solar cell, a polycrystalline silicon solar cell, a dye-sensitized solar cell, an organic thin-film solar cell, and so on.

[0075] Next, there will be explained an operation example of the electrochemical reaction device according to the embodiment. Here, the case where the gas containing carbon dioxide is supplied through the flow path **243** to produce carbon monoxide is explained as one example. In the anode part **10**, as expressed by the following formula (1), the water undergoes an oxidation reaction and loses electrons, and oxygen and hydrogen ions are produced. At least one of the produced hydrogen ions migrates to the cathode part **20** through the separator **30**.

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad (1)$$

[0076] In the cathode part **20**, as expressed by the following formula (2), the carbon dioxide undergoes a reduction reaction, and the hydrogen ions react with the carbon dioxide while receiving the electrons, and carbon monoxide and water are produced. Further, as expressed by the following formula (3), the hydrogen ions receive the electrons, and hydrogen is produced. At this time, the hydrogen may be produced simultaneously with the carbon monoxide.

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad (2)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (3)$$

[0077] The power supply **40** needs to have an open-circuit voltage equal to or more than a potential difference between a standard oxidation-reduction potential of the oxidation reaction and a standard oxidation-reduction potential of the reduction reaction. For example, the standard oxidation-reduction potential of the oxidation reaction in the formula (1) is 1.23 [V]. The standard oxidation-reduction potential of the reduction reaction in the formula (2) is 0.03 [V]. The standard oxidation-reduction potential of the reduction reaction in the formula (3) is 0 [V]. At this time, the open-circuit voltage needs to be 1.26 [V] or more in the reactions of the formula (1) and the formula (2).

[0078] As for the ion exchange membrane between the anode and the cathode, the carbon dioxide gas, carbonate ions, hydrogen carbonate ions, and so on sometimes impair the ion exchange membrane. Adjustment of the amount of carbon dioxide gas and the amount of vapor at this time enables extension of the life of the ion exchange membrane. However, under a condition of the hydrogen ions being present abundantly, generation of hydrogen occurs. Therefore, even with too many ions, applied energy is not used for the reduction reaction of the carbon dioxide, resulting in a decrease in reduction efficiency of the carbon dioxide. Therefore, it is necessary to maintain a balance between the amount of hydrogen ions required for the reduction of the carbon dioxide and suppression of the hydrogen generation.

[0079] The reduction reactions of hydrogen ions and carbon dioxide are reactions consuming hydrogen ions. This means that a small amount of the hydrogen ions results in low efficiency of the reduction reaction. Therefore, the first electrolytic solution and the second electrolytic solution preferably have different hydrogen ion concentrations so that the concentration difference facilitates the migration of the hydrogen ions. The concentration of anions (for example, hydroxide ions) may be made different between the electrolytic solution on the anode side and the electrolytic solution on the cathode side. When using a cation-exchange membrane as the ion exchange membrane, cations migrate, and when using an anion-exchange membrane as the ion exchange membrane, anions migrate. Further, in order to increase the concentration difference of the hydrogen ions, a method is considered, in which an inert gas not containing carbon dioxide (nitrogen, argon, or the like) is directly blown into the electrolytic solution, for example, to let the carbon dioxide contained in the electrolytic solution go, to thereby reduce the concentration of the hydrogen ions.

[0080] The reaction efficiency of the formula (2) varies depending on the concentration of the carbon dioxide dissolved in the electrolytic solution. The higher the concentration of the carbon dioxide, the higher the reaction efficiency, and as the former is lower, the latter is lower. The reaction efficiency of the formula (2) also varies depending on the concentration of the carbon dioxide and the vapor amount. As for these reactions, the porous conductive layer **23***a* is provided between the reduction catalyst layer **23***b* and the flow path **243** and the carbon dioxide is supplied through the porous conductive layer **23***a*, thereby making it possible to increase the concentration of the carbon dioxide in the electrolytic solution. Although the carbon dioxide is introduced into the flow path **243** in a gaseous form and the carbon dioxide is supplied to the reduction catalyst, by the water migrating from the anode **11** and the water produced by the reaction, the concentrations of the carbon dioxide and the water in the reduction catalyst layer **23***b* vary.

[0081] Unless a liquid component produced when reducing the carbon dioxide is efficiently discharged to the outside of the cathode part **20**, the porous conductive layer **23***a* and the reduction catalyst layer **23***b* are sometimes clogged with the liquid component to decrease the reaction efficiency. For example, when such an electrode material as a perforated metal or an expanded metal, which is often used for the cathode **23**, is used to form a type of obtaining both performances of gas and current collection, a decrease in the reaction efficiency is caused. Thus, the electrochemical reaction device according to this embodiment has a composition in which a flow path plate having a narrow tubular flow path is used and the generated liquid component is forced out by the flow path to be discharged. The flow path is formed by a plurality of flow paths disposed in parallel, a serpentine shaped flow path, or a combination thereof. Further, a distribution of the flow path with respect to a reaction surface is preferred to be uniform so that a uniform reaction can be performed on the cell surface.

[0082] The reduction catalyst for reducing the carbon dioxide varies in selectivity depending on the electrolyte, electrolyte membrane, or vapor pressure that is in contact therewith, and reduces the carbon dioxide to produce carbon monoxide, formic acid, ethylene, methane, and the like, but reduces protons depending on a condition to produce a large amount of hydrogen, resulting in a decrease in reduction efficiency of the carbon dioxide. This is because a proton source used for the reduction of the carbon dioxide is hydrogen ions or hydrogen carbonate ions, and the selectivity changes depending on, for example, the concentration of the hydrogen carbonate ions in the electrolytic solution or the pH. This change greatly affects the selectivity of carbon monoxide and hydrogen in a catalyst mainly using gold, and in a catalyst to perform a multielectron reduction of copper and the like, selectivities of carbon monoxide, formic acid, ethylene, methane, methanol, ethanol, formaldehyde, acetone, and so on are different from one another. Selecting the electrolytic solution becomes important for performing these controls. However, when the catalyst layer is in contact with the electrolyte membrane (or the electrolytic solution on the oxidation side) in order to reduce a cell resistance in the system of supplying the carbon dioxide gas to the reduction catalyst, the electrolytic solution is determined by compatibility with the oxidation catalyst, a cell resistance, or a balance of a composition of the electrolyte membrane, or the like with members forming the cell, so that it is difficult to select an optional electrolytic solution.

[0083] However, when the catalyst layer is in contact with the electrolyte membrane (or the electrolytic solution on the anode side) in order to reduce a cell resistance in the system of supplying the carbon dioxide gas to the reduction catalyst, the electrolytic solution is determined by compatibility with the oxidation catalyst, a cell resistance, or a balance of a composition of the electrolyte membrane, or the like with members forming the cell, so that it is difficult to select an optional electrolytic solution. Thus, changing the flow path structure also makes it possible to adjust the concentrations of the carbon dioxide and the water in the catalyst layer.

[0084] The production is not focused only on the reduction of carbon dioxide, and a reduced substance of carbon dioxide and hydrogen can also be produced at an arbitrary ratio in such a manner that, for example, carbon monoxide and hydrogen are produced at a ratio of 1:2, and through a chemical reaction performed thereafter, methanol is manufactured. The hydrogen is relatively easily obtainable by electrolyzing water, or is a fossil fuel-derived inexpensive raw material that is easily obtainable, so that the ratio of the hydrogen does not need to be large. Further, using the carbon dioxide as a raw material also contributes to a warming reduction effect, and thus when only the carbon monoxide can be reduced, environmental properties improve, but it is still difficult to efficiently cause a reaction. From the viewpoints of reaction efficiency, achievability, and a rate of the electrolyzing, a ratio of the carbon monoxide to the hydrogen is at least 1 or more and desirably 1.2 or more, and the ratio of 1.5 or more is preferred from the viewpoints of economic efficiency, environmental properties, and achievability.

[0085] The structure of the flow path plate **24** is not limited to the structure examples illustrated in FIG. **1** to FIG. **6**. FIG. **7** is a schematic top view of another structure example of the flow path plate **24**. FIG. **8** is a schematic cross-sectional view of a line segment **X1-Y1** in FIG. **7**. FIG. **9** is a schematic cross-sectional view of a line segment **X2-Y2** in FIG. **7**. In FIG. **7** to FIG. **9**, portions common to the structures illustrated in FIG. **1** to FIG. **6** can be assisted by the explanations in FIG. **1** to FIG. **6** as necessary.

[0086] The flow path plate illustrated in FIG. **7** to FIG. **9** includes a flow path layer **24***a* and a flow path layer **24***b* stacked on the flow path layer **24***a*. For the flow path layer **24***a* and the flow path layer **24***b*, high corrosion-resistant titanium, or the like can be used, but due to the relationship with press workability, price, or the like, working such as gold plating on a pressed plate of aluminum, SUS, or the like, conductive SUS for a high corrosion-resistant fuel cell, and the like may be used.

[0087] The flow path layer **24***a* includes the inflow port **243***a*, the outflow port **243***b*, an opening **245***a*, and an opening **245***b*. The inflow port **243***a* and the outflow port **243***b* are each provided to be exposed on a side surface of the flow path layer **24***a*.

[0088] The opening **245***a* penetrates the flow path layer **24***a* to communicate with the inflow port **243***a*. The opening **245***b* penetrates the flow path layer **24***a* to communicate with the outflow port **243***b*. The opening **245***a* and the opening **245***b* each may be formed by a groove.

[0089] The flow path layer **24***b* has a region **24***b***1** apart from the flow path layer **24***a* and a region **24***b***2** bent so as to project toward the flow path layer **24***a* from the region **24***b***1**. The region **24***b***1** may have therein an opening through which the flow path layer **24***b* penetrates.

[0090] The region **24***b***2** has an opening **246***a* and an opening **246***b*. The opening **246***a* communicates with the inflow port **243***a* through the opening **245***a*. The opening **246***b* communicates with the outflow port **243***b* through the opening **245***b*.

[0091] In the flow path plate illustrated in FIG. **7** to FIG. **9**, side surfaces of the flow path layer **24***a* and the flow path layer **24***b* are sealed by a sealing member **26**. At this time, the flow path **243** contains a space between the region **24***b***2** and the porous conductive layer **23***a* of the cathode **23**.

[0092] FIG. **10** is a schematic cross-sectional view illustrating another structure example of the electrochemical reaction device. The electrochemical reaction device illustrated in FIG. **10** includes a plurality of anodes **11**, a flow path plate **12**, a plurality of cathodes **23** each having a porous conductive layer **23***a* and a reduction catalyst layer **23***b*, a flow path plate **24** having a flow path layer **24***a* and a flow path layer **24***b*, a plurality of flow path layers **24***c*, a plurality of separators **30**, and a sealing member **26**. In FIG. **10**, a plurality of units each including the anode **11**, the cathode **23**, the separator **30**, and the flow path layer **24***c* are stacked. Parts common to the electrochemical reaction device explained with reference to FIG. **1** to FIG. **9** can be assisted by the explanations as necessary.

[0093] One of the anodes **11** is provided between one of the cathodes **23** and the flow path plate **12**. One of the cathodes **23** is provided between the above-described one of the anodes **11** and one of the flow path plates **24***c*. One of the separators **30** separates the above-described one of the anodes **11** from the above-described one of the cathodes **23**. One of the flow path layers **24***c* is provided between another of the cathodes **23** and the above-described one of the anodes **11**. Further, though not illustrated, the plural anodes **11** and the plural cathodes **23** are electrically connected to a power supply **40**.

[0094] The flow path plate **12** may be electrically connected to the power supply **40** via a current collector **13** similarly to the electrochemical reaction device illustrated in FIG. **1**, for example. The porous conductive layer **23***a* faces the flow path layer **24***c*. The reduction catalyst layer **23***b* faces the separator **30**.

[0095] The flow path layer **24***a* faces the porous conductive layer **23***a*. The flow path layer **24***a* may be electrically connected to the power supply **40** via a current collector **25** similarly to the electrochemical reaction device illustrated in FIG. **1**, for example. The flow path layer **24***b* is stacked on the flow path layer **24***a*. A region **24***b***1** of the flow path layer **24***b* has therein an opening through which the flow path layer **24***b* penetrates. For the flow path layer **24***c*, a flow path layer having the same structure as the flow path layer **24***a*, for example, can be used. Further, the electrochemical reaction device illustrated in FIG. **10** may have a structure in which the openings **246***a*, **246***b* of the flow path layer **24***a* are not provided and the region **24***b***2** extends to an end portion of the flow path layer **24***c*. At this time, carbon dioxide or an electrolytic solution may be directly supplied to the flow path **243** from the end portion of the flow path layer **24***c*. The flow path layer **24***c* is also referred to as a bipolar plate. Further, the sealing member **26** seals a stack of the above-described units.

[0096] In the electrochemical reaction device illustrated in FIG. **10**, an electrolytic solution on the anode **11** side and an electrolytic solution on the cathode **23** side can be made common, and further flow paths through which the electrolytic solution flows can be made common. For example, the same flow path layer **24***c* can be used as the flow path on the anode **11** side and the flow path on the cathode **23** side, and can also be used as a flow path on the cathode **23** side by having openings formed therein like the aforementioned flow path. Such a formation is preferred because the contact resistance between the anode **11** and the cathode **23** is reduced to improve the efficiency. Further, this formation is good because a cost reduction and a reduction in size and weight can be achieved by reducing the number of parts.

Example

Examples 1A, 1B, 2A, 2B, 3A, 3B, 4, 5, Comparative Examples 1, 2

[0097] A cell of an electrochemical reaction device in this example was fabricated as follows. An anode was formed by forming an oxidation catalyst containing an iridium oxide on a surface of a titanium-made wire mesh having a mesh structure by an etching method. Further, a cathode was fabricated by spraying 23 wt % of gold-carrying carbon onto a stack composed of a first porous conductive layer and a second porous conductive layer formed of a carbon paper to fabricate a catalyst layer-attached carbon paper with a gold-carrying amount being 0.2 mg/cm^2. The anode and the cathode were stacked with an ion exchange membrane (Nafion115) provided therebetween to fabricate a structure (catalyst area 400 mm^2).

[0098] A flow path plate on the cathode side was formed of conductive titanium. At a turned portion of a flow path, the flow path branches off into two in parallel connection. The number of branches at the turned portion is defined as a branch number, some of the branches including a confluence.

[0099] Values of respective parameters of flow path plates in Examples and Comparative examples are illustrated in Table 1. In Table 1, a reciprocation number means the number of turnbacks of the flow path. The reciprocation number being 1.5 means that the flow path extends so as to make two turnbacks. Further, the reciprocation number being 2.5 means that the flow path extends so as to make four turnbacks.

[0100] A flow path plate overlap length X indicates a length in the X-axis direction of an overlap of the flow path plate and the first or second porous conductive layer (corresponding to L1 in FIG. **3**). A flow path plate overlap length Y indicates a length in the Y-axis direction of the overlap of the flow path plate and the first or second porous conductive layer (corresponding to L2 in FIG. **3**). A flow path overlap length X indicates a length in the X-axis direction of an overlap of the flow path and the first or second porous conductive layer (corresponding to L**3** in FIG. **3**). A flow path overlap length Y indicates a length in the Y-axis direction of the overlap of the flow path and the first or second porous conductive layer (corresponding to L**4** in FIG. **3**). An overlap remainder length indicates the difference between the flow path plate overlap length Y and the flow path overlap length Y (corresponding to L**2**-L**4**). A flow path extended portion width indicates an average width of an extended portion of the flow path (corresponding to L**6** in FIG. **3**). A flow path turned portion width indicates an average width of the turned portion of the flow path (corresponding to L**8** in FIG. **8**). An inter-extended portion width indicates a width between one of the extended portions of the flow path and another of them (corresponding to L**9** in FIG. **3**). A flow path width ratio indicates a ratio of the extended portion width to the inter-extended portion width (corresponding to L**6**/L**9**). A flow path plate overlap end width X indicates the narrowest width between an end portion in the X-axis direction of a flow path plate overlap and a flow path overlap (corresponding to L**10** in FIG. **3**). A flow path plate overlap end width Y indicates the narrowest width between an end portion in the Y-axis direction of the flow path plate overlap and the flow path overlap (corresponding to L**11** in FIG. **3**).

[0101] A flow path cross-sectional area is obtained by the product (corresponding to L**6**×L**12**) of the width of the extended portion of the flow path and a depth of the flow path (corresponding to L**12** in FIG. **3**). A flow path overlap area indicates an area of the overlap of the flow path and the first or second porous conductive layer. The flow path overlap area is a value calculated by considering a curvature radius R of a corner of the flow path and defining a flow path shape. Concretely, the flow path overlap area is calculated by considering an angle of a corner with respect to the sum of a first area defined by the product of the length (L**5**) and the width (L**6**) of the extended portion of the flow path and a second area defined by the product of the length (L**7**) and the width (L**8**) of the turned portion.

[0102] An overlap remainder area indicates an area of the remainder of the overlap of the flow path plate and the first or second porous conductive layer from which the flow path overlap is removed. The overlap remainder area is a value obtained by subtracting an area of a polygon formed by connecting, out of vertexes of the overlap of the flow path and the first or second porous conductive layer, the vertexes each having an interior angle of less than 180 degrees from an area of the overlap. In this example, due to the first porous conductive layer and the second porous conductive layer both having one surface area of 400 mm^2, the value obtained by subtracting the area of the above-described polygon from 400 mm^2 was set as the value of the overlap remainder area.

[0103] A standard deviation a was calculated from a square root of a value obtained in a manner that the square of the shortest distance x between each of a plurality of intersection points of a plurality of first parting lines dividing the remainder of the flow path plate overlap from which the flow path overlap is removed along the X-axis direction by 0.1 mm each and a plurality of second parting lines dividing the above-described remainder along the Y-axis direction by 0.1 mm each and the overlap was calculated at each intersection point and the sum of the calculated squares of the shortest distances x was divided by an intersection point number n.

[0104] A number ratio indicates a number ratio of the number of intersection points, at which the shortest distance x is 0.5 mm or more, to the number n of all intersection points **83**. An area ratio indicates a ratio of an area of the overlap to an area of the overlap.

[0105] The flow path plate on the anode side is formed of conductive titanium. The flow path on the anode side extends along a contact surface with the carbon paper so as to make four turnbacks. The flow path has a structure similar to that of the flow path on the cathode side in a structure having nothing between the extended portions. The above-described structure was held sandwiched between the flow path plate on the anode side and the flow path plate on the cathode side to fabricate a cell of the electrochemical reaction device.

[0106] As an electrolytic solution, a 1.0 M potassium hydroxide solution was supplied to the flow path on the oxidation side of this cell at a flow rate of 0.6 sccm. A carbon dioxide gas was supplied to the flow path on the reduction side at a flow rate of 30 sccm. A 2.5 V voltage was applied between the anode and the cathode of this cell to collect gas generated from the cathode side, to then measure conversion efficiency of the carbon dioxide. Further, the generated gas was sampled and the quantity of the gas was identified and determined by gas chromatography. A current value on this occasion was measured by an ammeter. The current value, a partial current of carbon monoxide calculated from a generation amount of carbon monoxide, a partial current of hydrogen calculated from a generation amount of hydrogen, Faraday's efficiency of the carbon monoxide, Faraday's efficiency of the hydrogen, a production amount ratio of the carbon monoxide to the hydrogen (CO/H_2), and so on are illustrated in Table 1.

TABLE 1

	Example 1A	Example 1B	Example 2A	Example 2B	Example 3A	Example 3B	Example 4	Example 5	Comparative Example 1	Comparative Example 2
Flow Path Reciprocation Number [Time]	2.5	2.5	2.5	2.5	2.5	2.5	2.5	1.5	1.5	1.5
Flow Path Plate Overlap Length X (L1) [mm]	20	20	20	20	20	20	20	20	20	20
Flow Path Plate Overlap Length Y (L2) [mm]	20	20	20	20	20	20	20	20	20	20
Flow Path Overlap Length X (L3) [mm]	19	19	19	19	19	19	19	19	17	17.2
Flow Path Overlap Length Y (L4) [mm]	18.6	18.6	18.8	18.8	19.3	19.3	19.4	19	16.5	18.4
Overlap Remainder Length (L2 − L4) [mm]	1.4	1.4	1.2	1.2	0.7	0.7	0.6	1	3.5	1.6
Flow Path Extended Portion Width (L6) [mm]	1.5	1.5	1.7	1.7	1.3	1.3	1.4	1.5	1.5	1.4
Flow Path Turned Portion Width (L8) [mm]	2	2	2	2	2	2	2	2	2	2

TABLE 1-continued

	Example 1A	Example 1B	Example 2A	Example 2B	Example 3A	Example 3B	Example 4	Example 5	Comparative Example 1	Comparative Example 2
Inter-Extended Portion Width (L9) [mm]	0.40	0.40	0.20	0.20	0.70	0.70	0.60	2.00	1.50	1.40
Flow Path Width Ratio (L6/L9)	3.75	3.75	8.5	8.5	1.86	1.86	2.33	0.75	1	0.7
Flow Path Plate Overlap End Width X (L10) [mm]	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1.5	1.4
Flow Path Plate Overlap End Width Y(L11) [mm]	0.7	0.7	0.6	0.6	0.35	0.35	0.3	0.5	1.75	0.8
Flow Path Cross-Sectional Area [mm^2]	3	3	3.4	3.4	2.6	2.6	2.8	3	3	2.8
Flow Path Overlap Area [mm^2]	293.6	293.6	326	326	264	280	264	200.4	175.3	174.8
Overlap Remainder Area [mm^2]	23.3	23.3	21.4	21.4	16.65	15.7	16.65	19.5	59.75	41.76
Standard Deviation σ	0.679	0.679	0.695	0.695	0.663	0.663	0.663	0.729	0.906	0.796
Number Ratio [%]	6	6	6	6	0	0	0	0	59.75	33
Area Ratio	0.734	0.734	0.815	0.815	0.66	0.66	0.701	0.501	0.438	0.437
Overall Current [mA]	110	110	120	130	130	135	125	110	100	100
H_2 Partial Current [mA]	68	56	72	66	43	57	47	52	64	66
Co Partial Current (mA)	54	51	48	55	70	89	62	46	15	23
H_2 Faraday's Efficiency [%]	62	51	60	51	33	35	46	47	64	66
Co Faraday's Efficiency [%]	49	46	40	43	54	49	66	42	15	23
Production Amount Ratio	0.8	0.9	0.67	0.84	1.64	1.9	1.08	0.88	0.23	0.35

[0107] FIG. **11** is a view illustrating the relationship between an area ratio of an area of an overlap of the first or second porous conductive layer and the flow path to an area of an overlap of the first or second porous conductive layer and the flow path plate and the Faraday's efficiency. In FIG. **11**, each square mark indicates the relationship between the area ratio and the Faraday's efficiency of the hydrogen, and each triangle mark indicates the relationship between the area ratio and the Faraday's efficiency of the carbon monoxide.

[0108] FIG. **12** is a view illustrating the relationship between the above-described area ratio and the overall current or the partial current. In FIG. **12**, each square mark indicates the relationship between the area ratio and the partial current of the hydrogen, each triangle mark indicates the relationship between the area ratio and the partial current of the carbon monoxide, and each rhombus mark indicates the relationship between the area ratio and the overall current.

[0109] As illustrated in FIG. **11** and FIG. **12**, when the area ratio is about 0.65, the Faraday's efficiency of the hydrogen, the Faraday's efficiency of the carbon monoxide, a Faraday's efficiency ratio, the overall current, and the partial current of the carbon monoxide each exhibit a high value, and the area ratio needs to be 0.5 or more in order for the overall current value to be greater than 100 mA. A high current density per area means a high reaction density and high cell performance efficiency. Furthermore, when the area ratio is 0.5 or more and 0.85 or less, the partial current of the carbon monoxide becomes 45 mA or more, and further when the area ratio is 0.5 or more and 0.85 or less, the practical Faraday's efficiency becomes 40% or more and CO/H_2 becomes 0.6 or more, which indicates that the area ratio needs to be 0.5 or more and 0.85 or less from the practical viewpoint.

[0110] FIG. **13** is a view illustrating the relationship between the flow path width ratio and the overall current or the partial current. In FIG. **13**, each square mark indicates the relationship between the flow path width ratio and the partial current of the hydrogen, each triangle mark indicates the relationship between the flow path width ratio and the partial current of the carbon monoxide, and each rhombus mark indicates the relationship between the flow path width ratio and the overall current. When the flow path width ratio is 1.9, the overall current exhibits a high value, which reveals that it becomes difficult to obtain 45 mA or more of the partial current of the carbon monoxide as long as the flow path width ratio is at least 1.5 or more and 5 or less. As long as the width between the extended portions of the flow path is also wide, reaction selectivity of the carbon monoxide improves and the partial current of the carbon monoxide also increases. In the case of the reciprocation number being 1.5, the partial current of the carbon monoxide is high, but the overall current is low.

[0111] FIG. **14** is a view illustrating the relationship between the overlap remainder area and the overall current or the partial current. In FIG. **14**, each square mark indicates the relationship between the overlap remainder area and the partial current of the hydrogen, each triangle mark indicates the relationship between the overlap remainder area and the partial current of the carbon monoxide, and each rhombus mark indicates the relationship between the overlap remainder area and the overall current. In a region with the overlap remainder area being 25 mm^2 or less, the partial current of the carbon monoxide is 45 mA or more. This reveals that the ratio of the area of the overlap remainder to the area of one surface of the first or second porous conductive layer is preferred to be ⅙ or less.

[0112] A comparison between Comparative example 1 and Comparative example 2 reveals that the flow path areas are almost the same and in Comparative example 1, the inter-extended portion width is wide and the remainder area is small. Further, the Faraday's efficiency of the carbon monoxide is 15% in Comparative example 1 and 23% in Comparative example 2, and the partial current is 15 mA in Comparative example 1 and 23 mA in Comparative example 2. The overall current values are almost the same, to thus reveal that Comparative example 2 is higher in the cell performance than Comparative example 1. This is because the contribution of the efficiency improvement due to the overlap remainder area being small rather than the inter-extended portion width being narrow was large. This is because in the case of the shortest distance between the overlap end portion and the overlap being long, the concentration of water inside the first porous conductive layer increases to generate hydrogen greatly.

[0113] In Comparative example 1, the extended portion width and the inter-extended portion width is each 1.5 mm, while in Comparative example 2, the extended portion width is 1.4 mm and the inter-extended portion width is 2 mm. It is possible to confirm that the reaction selectivity of the carbon monoxide is higher in Comparative example 2 even though the structure having a wide inter-extended portion width is disadvantageous to the selectivity of the carbon monoxide. This is because in Comparative example 2, of the flow path overlap, the length in the X-axis direction is 17 mm and the length in the Y-axis direction is 16.5 mm, to thus extremely increase the remainder area. However, the efficiency is low and the formation of Comparative example 2 is not preferred practically.

[0114] In an actual cell, the reaction is caused on a cell area of about 100 cm^2, so that the ratio of the overlap remainder area to the area of the overlap is small to reduce the effect. As a result of calculation considering the fact that the size of a cell to be used actually is 7 cm square or more, the ratio of the overlap remainder area to the area of the overlap needs to be 0.7 or less in order for at least the width of the remainder to be 1.5 mm or less, and it can be said that the ratio being equal to or less than this is effective for the cell performance improvement.

[0115] FIG. **15** is a view illustrating the relationship between the standard deviation a and the overall current or the partial current. In FIG. **15**, each square mark indicates the relationship between the standard deviation a and the partial current of the hydrogen, each triangle mark indicates the relationship between the standard deviation a and the partial current of the carbon monoxide, and each rhombus mark indicates the relationship between the standard deviation a and the overall current. FIG. **15** reveals that the standard deviation a is preferred to be 0.8 or less. Further, the standard deviation a is preferred to be 0.75 or less in order that the Faraday's efficiency of the carbon monoxide may become 40% or more, the partial current value of the carbon monoxide may become about 50 mA, and the production amount ratio of the carbon monoxide to the hydrogen may become 1:1 or more.

[0116] FIG. **16** is a view illustrating the relationship between the number ratio of the intersection point, at which the shortest distance between the intersection point of the first parting line and the second parting line and the flow path overlap is 0.5 mm or more, and the overall current or the partial current. In FIG. **16**, each square mark indicates the relationship between the number ratio and the partial current of the hydrogen, each triangle mark indicates the relationship between the number ratio and the partial current of the carbon monoxide, and each rhombus mark indicates the relationship between the number ratio and the overall current. As illustrated in FIG. **16**, it is found out that in the case of the number ratio being greater than 30%, the hydrogen is generated greatly and the production amount of the carbon monoxide is extremely small, and thus, the number ratio is preferred to be at least 30% or less. It is more preferably 20% or less and desirably 10% or less, resulting in that it is preferred because the Faraday's efficiency of the carbon monoxide becomes about 50%.

[0117] In these examples and the comparative examples, the flow path extending in a serpentine shape was used so that effects of a side flow caused by the flow path structure and a power generation distribution in the cell could be suppressed, and in a region with a large flow rate of the carbon dioxide, a comparison was made among these examples and the comparative examples in the flow path structure and thereby a comparison was made in the flow path area and other parameters. However, the reaction selectivity varies depending on the concentrations of the water and the carbon dioxide in the first porous conductive layer in the cell, and therefore the similar effect can be obtained not only with the flow path in a serpentine shape, but also with other flow paths in a lattice shape, and the like.

[0118] Further, these ratios and tendencies vary also depending on the catalyst and the gas diffusion layer, and changing the catalyst and the solution components also makes it possible to change the products and the ratios. As a result of changing the gas diffusion layer to recognize the difference according to the flow path structure, a preferred positional relationship of electrolysis efficiency of the carbon monoxide does not change greatly and similar effects are recognized. This is because a tendency of a concentration distribution of the carbon dioxide in a lower portion of the flow path and a tendency of a concentration distribution of the water in a lower portion of a region between the extended portions are similar. As values resulting from reduction of water repellency of the gas diffusion layer, the overall current value and the selectivity of the carbon monoxide tend to decrease, but in the graph shape, similar values are illustrated in terms of a peak position of the partial current value of the electrolysis of the carbon monoxide and a range of the Faraday's efficiency and similar effects are exhibited. As for a cell voltage similarly, in the case of a lower voltage, the total value decreases and the ratio of the carbon monoxide tends to increase, but similar effects are recognized also from the viewpoint of a partial current density of the reduction of the carbon dioxide. In the case of a high voltage, the total value increases and the ratio of the carbon monoxide tends to decrease, but a similar tendency is recognized regarding a preferred position of the partial current density of the reduction of the carbon dioxide. Further, also in the reduction reaction of the carbon dioxide using a copper catalyst, similar tendencies are obtained in terms of each of the overall current density, the Faraday's efficiency, and the overall current value of the hydrogen and the carbon dioxide.

[0119] While certain embodiments have been described, these embodiments have been presented by way of example only, and are not intended to limit the scope of the inventions. Indeed, the novel embodiments described herein may be embodied in a variety of other forms; furthermore, various omissions, substitutions and changes in the form of the embodiments described herein may be made without departing from the spirit of the inventions. The accompanying claims and their equivalents are intended to cover such forms or modifications as would fall within the scope and spirit of the inventions.

What is claimed is:

1. An electrochemical reaction device, comprising:

an anode to oxidize water and thus generate oxygen;

an electrolytic solution flow path facing on the anode and through which an electrolytic solution containing the water flows;

a cathode including: a porous conductive layer having a first surface and a second surface; and a reduction catalyst layer having a third surface disposed on the first surface and containing a reduction catalyst to reduce carbon dioxide and thus generate a carbon compound;

a separator between the anode and the cathode;

a power supply connected to the anode and the cathode; and

a flow path plate including: a fourth surface on the second surface; and a flow path facing on the second surface and through which the carbon dioxide flows,

wherein a ratio of an area of an overlap of the second surface and the flow path to an area of the second surface is 0.5 or more and 0.85 or less.

2. The device according to claim **1**,

wherein a ratio of an area of an overlap of the third surface and the flow path to an area of the third surface is 0.5 or more and 0.85 or less.

3. The device according to claim **1**,

wherein the flow path has a first region, a second region, and a third region, the first region extending on the fourth surface, the third region extending along the first region, and the second region extending and bending from the first region to the third region,

a ratio of an average width of the first region to an average width between the first and third regions is 1.5 or more and 5 or less.

4. The device according to claim **1**,

wherein if the second surface is divided into a polygonal portion and a remainder portion, the polygonal portion is formed by connecting vertexes of the overlap of the second surface and the flow path, each of interior angles of the overlap thereof corresponding to the vertexes is less than 180 degrees, and a ratio of an area of the remainder portion to the area of the second surface is ⅙ or less.

5. The device according to claim **1**,

wherein if the second surface is divided into a polygonal portion and a remainder portion, the polygonal portion is formed by connecting vertexes of the overlap of the third surface and the flow path, each of interior angles of the overlap thereof corresponding to the vertexes is less than 180 degrees, and a ratio of an area of the remainder portion to the area of the third surface is ⅙ or less.

6. The device according to claim **1**,

wherein if an overlap of the second and fourth surfaces is divided along first lines and second lines except for the overlap of the second surface and the flow path, the first lines are away from each other along a first direction of the fourth surface at intervals of 0.1 mm, the second lines are away from each other along a second direction perpendicular to the first direction along the fourth surface at intervals of 0.1 mm, the first lines and the second lines cross each other to define intersection points, and a standard deviation of shortest distances between each of the intersection points and the overlap of the second surface and the flow path is 0.8 or less.

7. The device according to claim **1**,

wherein if an overlap of the third and fourth surfaces is divided along first lines and second lines except for the overlap of the third surface and the flow path, the first lines are away from each other along a first direction of the fourth surface at intervals of 0.1 mm, the second lines are away from each other along a second direction perpendicular to the first direction along the fourth surface at intervals of 0.1 mm, the first lines and the second lines cross each other to define intersection points, and a standard deviation of shortest distances between each of the intersection points and the overlap of the third surface and the flow path is 0.8 or less.

8. The device according to claim **1**,

wherein if an overlap of the second and fourth surfaces is divided along first lines and second lines except for the overlap of the second surface and the flow path, the first lines are away from each other along a first direction of the fourth surface at intervals of 0.1 mm, the second lines are away from each other along a second direction perpendicular to the first direction along the fourth surface at intervals of 0.1 mm, the first lines and the second lines cross each other to define intersection points, and shortest distances between each of 30% or less of the intersection points in a number ratio and the overlap of the second surface and the flow path is 0.5 mm or more.

9. The device according to claim **1**,

wherein if an overlap of the third and fourth surfaces is divided along first lines and second lines except for the overlap of the third surface and the flow path, the first lines are away from each other along a first direction of the third surface at intervals of 0.1 mm, the second lines are away from each other along a second direction perpendicular to the first direction along the third surface at intervals of 0.1 mm, the first lines and the second lines cross each other to define intersection points, and shortest distances between each of 30% or less of the intersection points in a number ratio and the overlap of the third surface and the flow path is 0.5 mm or more.

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