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(54) **METHANOL GENERATION DEVICE, METHOD FOR GENERATING METHANOL, AND ELECTRODE FOR GENERATING METHANOL**

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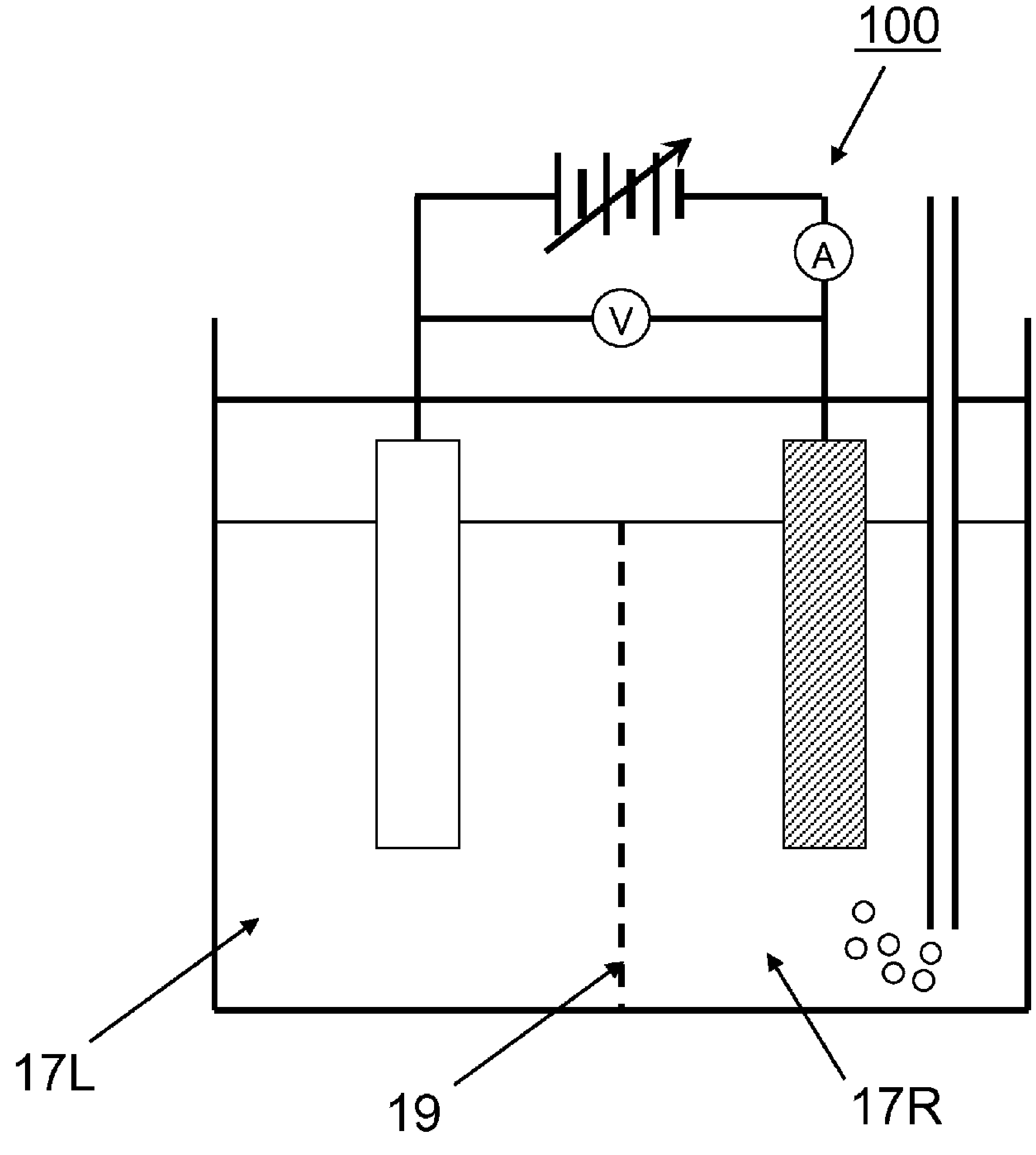
(57) **ABSTRACT**

The present invention provides a methanol generation device for generating methanol by reducing carbon dioxide, comprising: a container for storing an electrolyte solution containing carbon dioxide; a cathode electrode disposed in the container so as to be in contact with the electrolyte solution; an anode electrode disposed in the container so as to be in contact with the electrolyte solution; and an external power supply for applying a voltage so that a potential of the cathode electrode is negative with respect to a potential of the anode electrode. The cathode electrode has a region of $Cu_{1-x-y}Ni_xAu_y$ ($0<x$, $0<y$, and $x+y<1$). The anode electrode has a region of a metal or a metal compound.



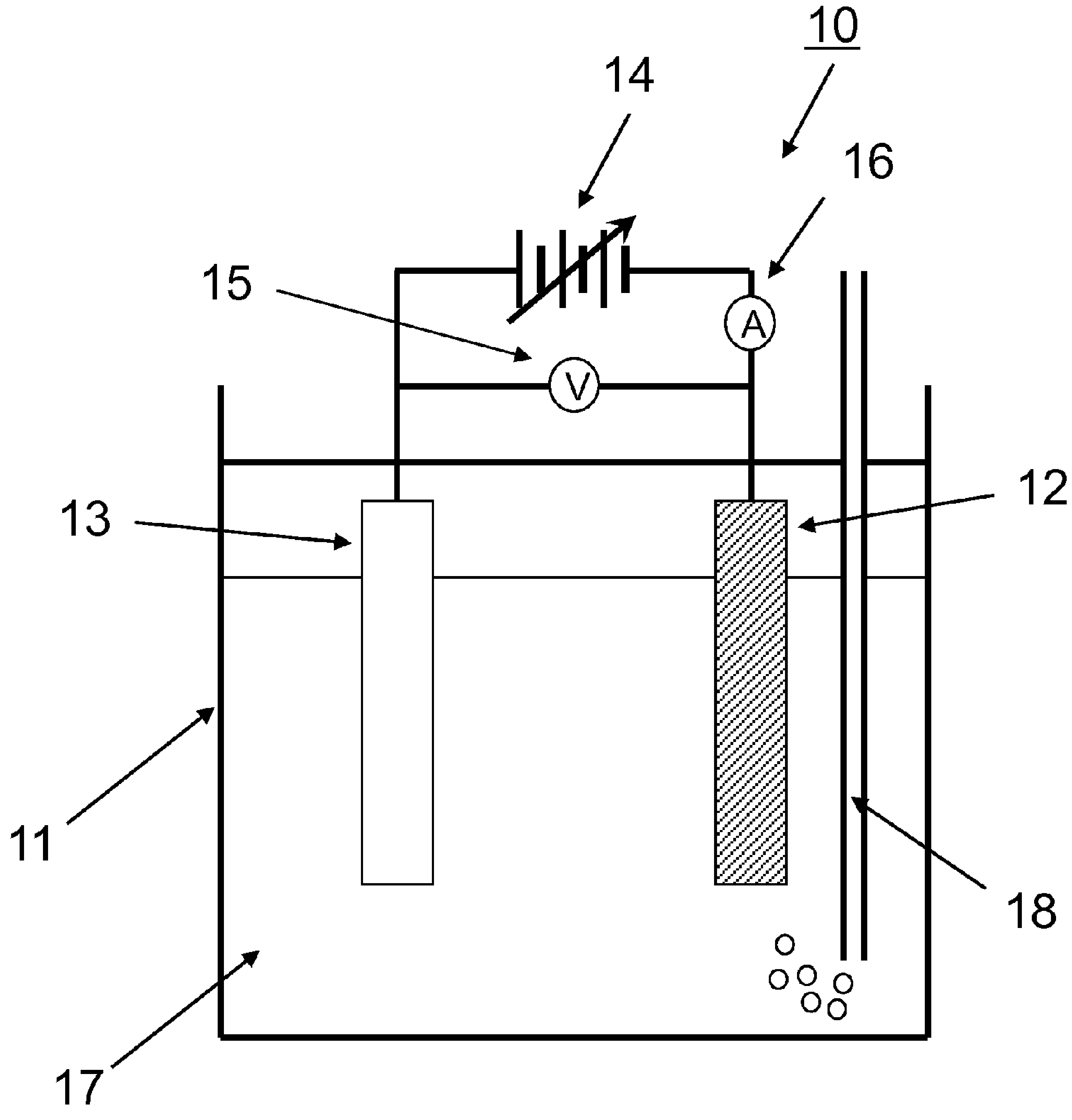


FIG. 1A

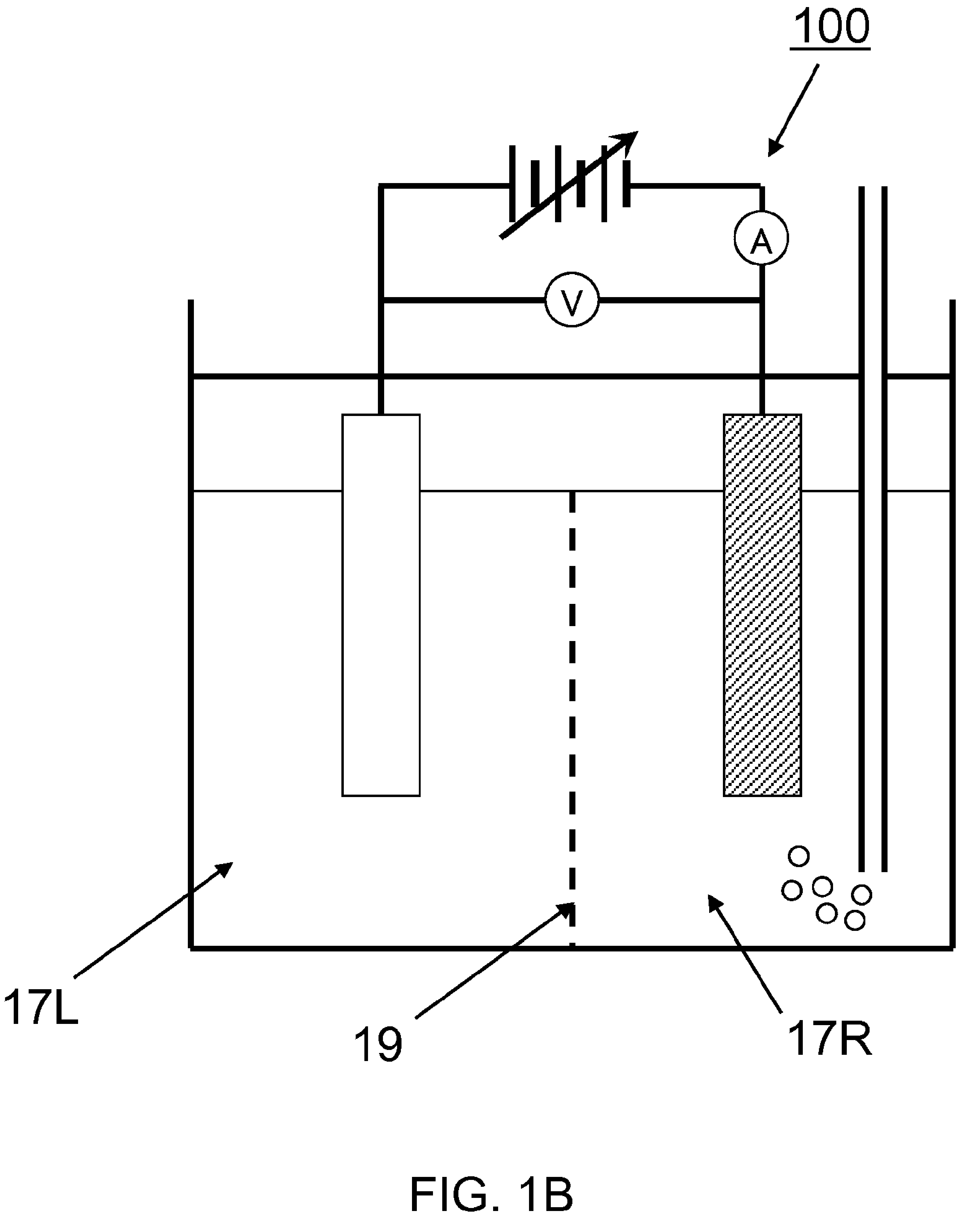


FIG. 1B

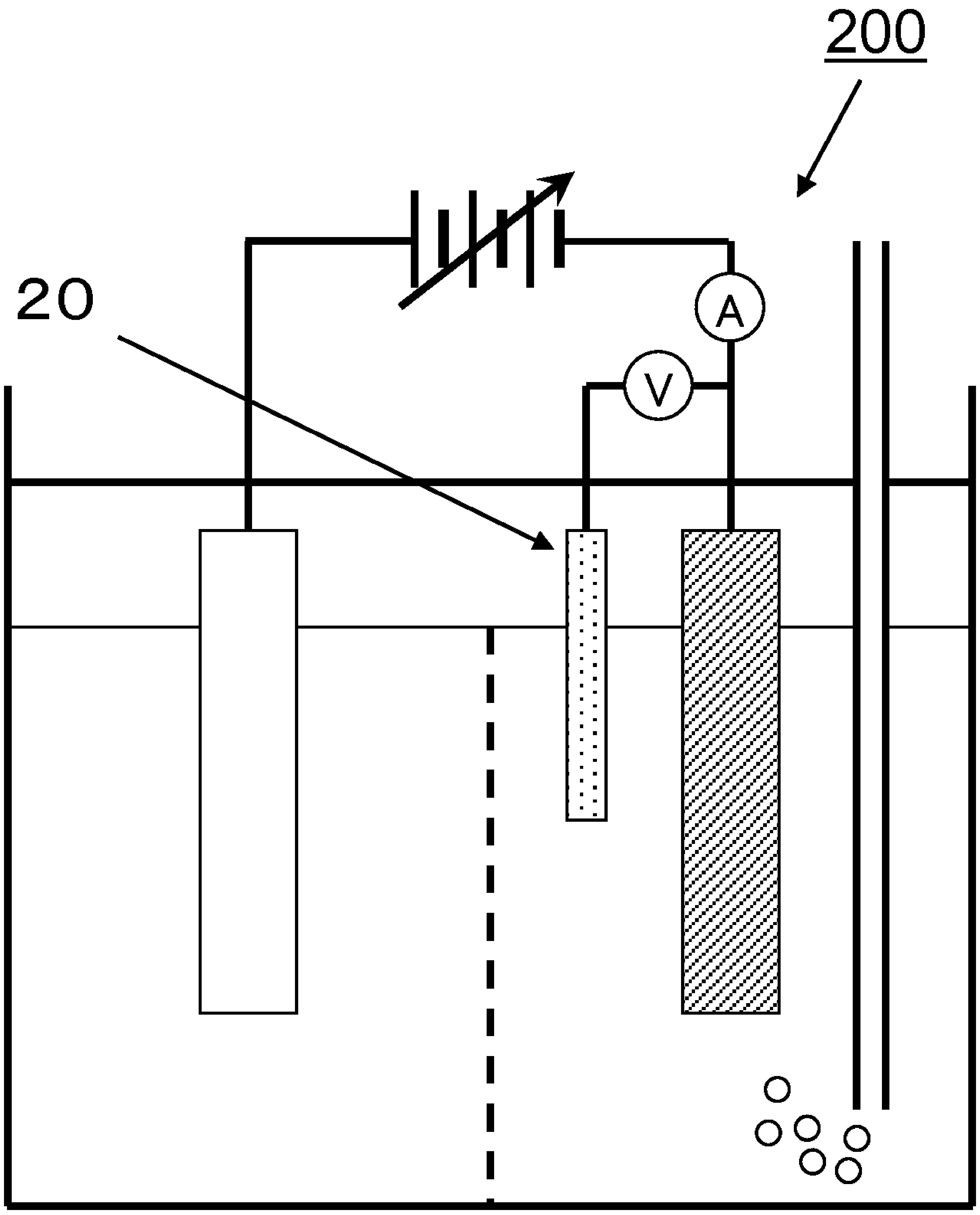


FIG. 1C

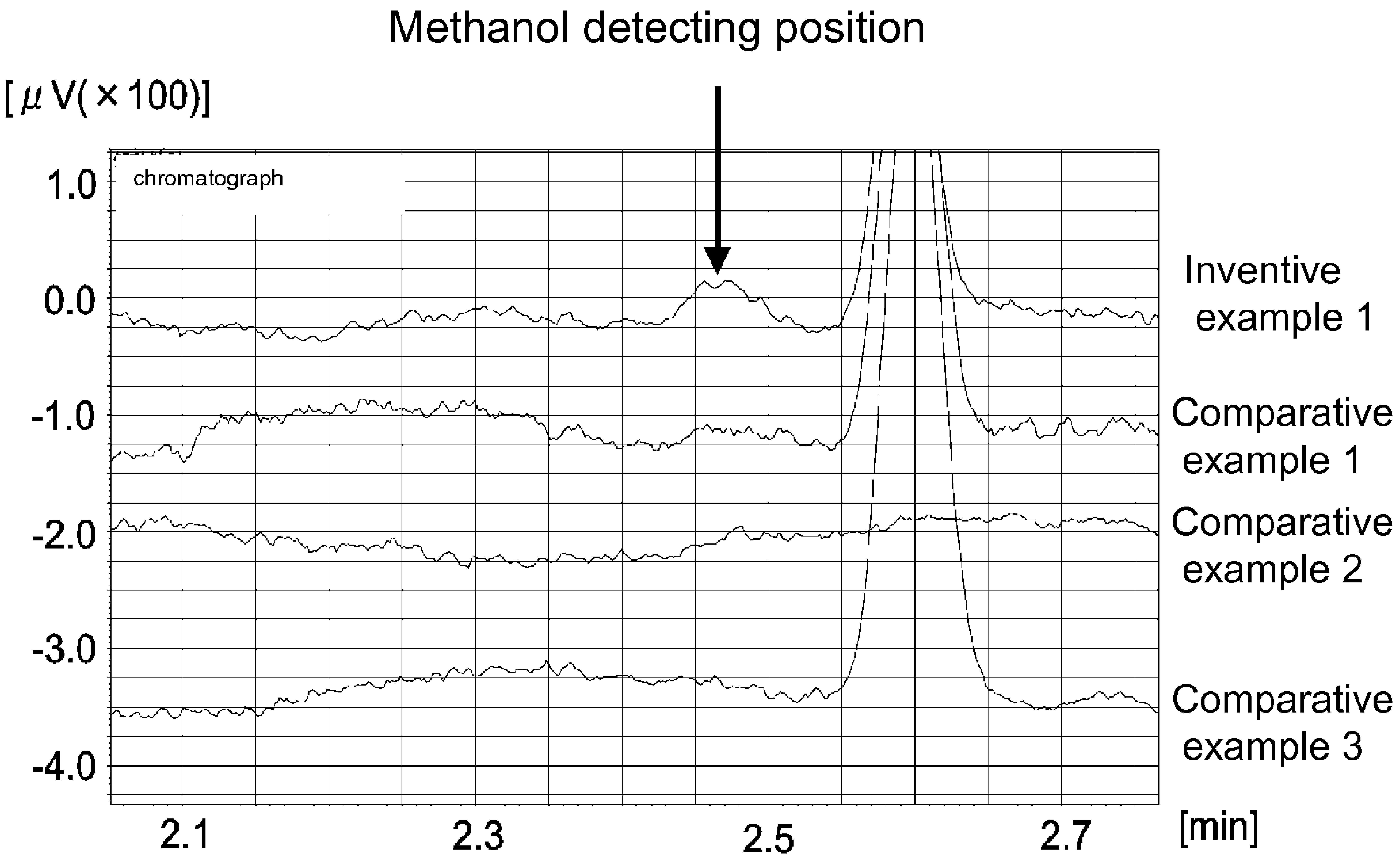

Methanol detecting position
[μV(×100)]
chromatograph
1.0
0.0
-1.0
-2.0
-3.0
-4.0
Inventive example 1
Comparative example 1
Comparative example 2
Comparative example 3
2.1
2.3
2.5
2.7
[min]

FIG. 2

METHANOL GENERATION DEVICE, METHOD FOR GENERATING METHANOL, AND ELECTRODE FOR GENERATING METHANOL

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This is a continuation of International Application No. PCT/JP2014/003030, with an international filing date of Jun. 6, 2014, which claims priority of Japanese Patent Application No. 2013-135824, filed on Jun. 28, 2013, the contents of which are hereby incorporated by reference.

BACKGROUND

[0002] 1. Technical Field

[0003] The present disclosure relates to a methanol generation device, a method for generating methanol, and an electrode for generating methanol.

[0004] 2. Description of the Related Art

[0005] Japanese Patent Application laid-open Publication No. 2000-254508A, Japanese Patent Application laid-open Publication No. Hei 1-313313A, U.S. Pat. No. 5,234,768, Japanese Patent Application laid-open Publication No. 2004-176129A, and Y. Hori, "Modern Aspects of Electrochemistry", 2008, vol. 42, p.p. 89-189 disclose a method for reducing carbon dioxide.

[0006] Japanese Patent Application laid-open Publication No. 2000-254508A and Japanese Patent Application laid-open Publication No. Hei 1-313313A disclose a method for reducing carbon dioxide using a gas phase reaction performed under high temperature.

[0007] U.S. Pat. No. 5,234,768 discloses a method for reducing carbon dioxide electrochemically using a phthalocyanine metal complex.

[0008] Japanese Patent Application laid-open Publication No. 2004-176129A, Y. Hori, "Electrochemical CO2 Reduction on Metal Electrodes", Modern Aspects of Electrochemistry, 2008, vol. 42, p.p. 89-189, and Y. Hori et. al. "Nickel and Iron Modified Copper Electrode for Electroreduction of CO_2 by In-situ Electrodeposition", Chemistry Letters, pp. 1567-1570, 1989 disclose a method for reducing carbon dioxide electrochemically using metal copper, copper halide or nickel-plated copper.

SUMMARY

[0009] The present invention provides a methanol generation device for generating methanol by reducing carbon dioxide, comprising:

[0010] a container for storing an electrolyte solution containing carbon dioxide;

[0011] a cathode electrode disposed in the container so as to be in contact with the electrolyte solution;

[0012] an anode electrode disposed in the container so as to be in contact with the electrolyte solution; and

[0013] an external power supply for applying a voltage so that a potential of the cathode electrode is negative with respect to a potential of the anode electrode;

[0014] wherein

[0015] the cathode electrode has a region of $Cu_{1-x-y}Ni_xAu_y$ ($0<x$, $0<y$, and $x+y<1$); and the anode electrode has a region of a metal or a metal compound.

[0016] The present invention provides a methanol generation device having high methanol generation efficiency.

[0017] Other features, elements, processes, steps, characteristics and advantages of the present invention will become more apparent from the following detailed description of preferred embodiments of the present invention with reference to the attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. **1**A shows a schematic view of a methanol generation device according to the present disclosure.

[0019] FIG. **1**B shows a schematic view of a methanol generation device according to the present disclosure.

[0020] FIG. **1**C shows a schematic view of a methanol generation device according to the present disclosure.

[0021] FIG. **2** is a graph showing results of the inventive example 1 and the comparative examples 1-2.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0022] The embodiments of the methanol generation device and method for generating methanol according to the present disclosure will be described with reference to the drawings.

Methanol Generation Device

[0023] FIG. **1**A-FIG. **1**C each show a schematic view of a methanol generation device for generating methanol by reducing carbon dioxide.

[0024] A methanol generation device **10** comprises a container **11**, a cathode electrode **12**, an anode electrode **13**, and an external power supply **14**. As shown in FIG. **1**A, the methanol generation device **10** may have a voltage measurement device **15** and a current measurement device **16**, each of which is used to monitor how carbon dioxide is reduced.

[0025] An electrolyte solution **17** is stored in the container **11**. As one example, the electrolyte solution **17** is a potassium chloride aqueous solution, a sodium chloride aqueous solution, a sodium hydrogen carbonate aqueous solution, or a sodium sulfate aqueous solution. In particular, a potassium chloride aqueous solution or a sodium chloride aqueous solution is desirable. It is desirable that the electrolyte solution **17** has a concentration of not less than 0.05 mol/L and not more than 5.0 mol/L.

[0026] The cathode electrode **12** has CuNiAu which is a copper-nickel-gold alloy. Hereinafter, copper is referred to as "Cu", nickel is referred to as "Ni", and gold is referred to as "Au". CuNiAu has a composition formula of $Cu_{1-x-y}Ni_xAu_y$ (where $0<x$, $0<y$, and $x+y<1$).

[0027] It is desirable that CuNiAu is in a state of a solid solution or an intermetallic compound. The solid solution means an alloy in which the elements constituting the alloy are randomly mixed at the atomic level. The intermetallic compound means a compound in which the elements constituting the compound are arranged regularly at the atomic level.

[0028] An example of a method for fabricating CuNiAu in the state of the solid solution is a vacuum melting method or an arc melting method. The value of x in the composition formula $Cu_{1-x-y}Ni_xAu_y$ represents the composition ratio of Ni to CuNiAu. The value of y in the composition formula $Cu_{1-x-y}Ni_xAu_y$ represents the composition ratio of Au to CuNiAu. It is desirable that the value of x is more than 0 and not more than 0.50 and the value of y is not less than 0.001 and not more than 0.10. In particular, it is more desirable that the value of x is more than 0 and not more than 0.20 and the value of y is not less than 0.005 and not more than 0.05.

[0029] CuNiAu which constitutes the cathode electrode **12** may contain elements other than Cu, Ni and Au, as long as the crystalline structure of CuNiAu is free from disturbance. CuNiAu fabricated by a vacuum melting method or an arc melting method may contain impurities at a normally acceptable level. The crystalline structure of CuNiAu can be observed, for example, by conducting an X-ray diffraction measurement. An example of a method for measuring the composition ratio of each element contained in the alloy is an energy dispersive X-ray analysis method. In this method, the measurement limit value of Ni is approximately 0.1% at an atomic ratio.

[0030] The cathode electrode **12** may be composed only of CuNiAu; however, the cathode electrode **12** may have a stacked structure having a CuNiAu layer and a substrate for supporting the CuNiAu layer. For example, the cathode electrode **12** is a stacked structure obtained by forming a CuNiAu thin film on the substrate formed of glass or glassy carbon. Instead, the cathode electrode **12** may be formed by arranging a lot of CuNiAu fine particles on a conductive substrate. The cathode electrode **12** is not limited, as long as the cathode electrode **12** is capable of reducing carbon dioxide and generating methanol.

[0031] The cathode electrode **12** is in contact with the electrolyte solution **17**. More accurately, CuNiAu contained in the cathode electrode **12** is in contact with the electrolyte solution **17**. As long as CuNiAu is in contact with the electrolyte solution **17**, only a part of the cathode electrode **12** has to be immersed in the electrolyte solution **17**.

[0032] The anode electrode **13** has a conductive material. An example of the conductive material is carbon, platinum, gold, silver, copper, titanium, iridium oxide, or an alloy thereof. The conductive material is not limited, as long as the conductive material is not decomposed through the oxidation reaction of the conductive material itself.

[0033] The oxidation reaction of water performed in the anode electrode **13** is independent of the reduction reaction of carbon dioxide performed in the cathode electrode **12**. The material of the anode electrode **13** does not have an influence on the reaction performed on the cathode electrode **12**.

[0034] The anode electrode **13** is also in contact with the electrolyte solution **17**. More accurately, the conductive material included in the anode electrode **13** is in contact with the electrolyte solution **17**. As long as the conductive material is in contact with the electrolyte solution **17**, only a part of the anode electrode **13** has to be immersed in the electrolyte solution **17**.

[0035] As shown in FIG. **1**A, the methanol generation device **10** may have a tube **18** in the container **11**. Carbon dioxide may be supplied through the tube **18** to the electrolyte solution **17**. One end of the tube **18** is immersed in the electrolyte solution **17**.

[0036] As shown in FIG. **1**B, a methanol generation device **100** may comprise a solid electrolyte membrane **19** in the container **11**. The solid electrolyte membrane **19** divides the electrolyte solution **17** into an anode-side electrolyte solution **17**L and a cathode-side electrolyte solution **17**R. In other words, the solid electrolyte membrane **19** divides the inside of the container **11** into an anode container for storing the anode-side electrolyte solution **17**L and a cathode container for storing the cathode-side electrolyte solution **17**R.

[0037] The solid electrolyte membrane **19** prevents the anode-side electrolyte solution **17**L and the cathode-side electrolyte solution **17**R from being mixed with each other. Since the solid electrolyte membrane **19** allows passage of protons therethrough, the solid electrolyte membrane **19** connects the cathode-side electrolyte solution **17**R with the anode-side electrolyte solution **17**L electrically. An example of the solid electrolyte membrane **19** is a Nafion membrane available from Du Pont. The reason why the electrolyte solution **17** is divided using the solid electrolyte membrane **19** will be described later.

[0038] As shown in FIG. **1**C, a methanol generation device **200** may comprise a reference electrode **20** near the cathode electrode **12**. The reference electrode **20** is in contact with the cathode-side electrolyte solution **17**R. The reference electrode **20** is used for measuring the electric potential of the cathode electrode **12** and is connected to the cathode electrode **12** through the voltage measurement device **15**. An example of the reference electrode **20** is a silver/silver chloride electrode (hereinafter, referred to as "Ag/AgCl electrode").

Method for Generating Methanol

[0039] A method for generating methanol using the abovementioned methanol generation device will be described below.

[0040] The methanol generation device may be placed under room temperature and atmospheric pressure.

[0041] A voltage is applied to the cathode electrode **12** using the external power supply **14** so that the voltage is negative with respect to the potential of the anode electrode **13**. A voltage exceeding a threshold for establishing the methanol generation reaction has to be applied using the external power supply **14**. The threshold varies depending on the interval between the cathode electrode **12** and the anode electrode **13**, the materials constituting the cathode electrode **12** and the anode electrode **13**, and the concentration of the electrolyte solution **17**. It is desirable that the threshold is not less than 2.5 volts.

[0042] A part of the electric energy applied to the cathode electrode **12** with respect to the anode electrode **13** is consumed for the oxidization reaction of water which occurs on the anode electrode **13**. For this reason, in the case of using the methanol generation device shown in FIG. **1**A or FIG. **1**B, it is difficult to know the actual voltage applied to the cathode electrode **12**. On the other hand, in the case of using the methanol generation device shown in FIG. **1**C, the actual voltage applied to the cathode electrode **12** can be determined accurately. The potential of the cathode electrode **12** with respect to the potential of the reference electrode **20** may vary depending on the materials of the reference electrode **20**. It is desirable that the potential of the cathode electrode **12** with respect to the potential of the reference electrode **20** is not more than −1.7 volts.

[0043] As just described, by applying an appropriate voltage to the cathode electrode **12**, the carbon dioxide contained in the electrolyte solution **17** is reduced on the cathode electrode **12**. As a result, methanol is generated on the surface of the cathode electrode **12**.

[0044] On the other hand, oxygen is generated on the anode electrode **13** through the oxidization reaction of water. In a case where the electrolyte solution **17** contains methanol, not only water but also methanol is oxidized. In other words, a part of the methanol generated on the cathode electrode **12**

may reach the anode electrode **13**, and oxidized on the anode electrode **13**. As a result, the generated methanol is returned to carbon dioxide. In order to prevent such a reverse reaction, as shown in FIG. **1**B and FIG. **1**C, the cathode-side electrolyte solution **17**R and the anode-side electrolyte solution **17**L are preferably separated from each other using the solid electrolyte membrane **19**.

[0045] A reaction current flows through the cathode electrode **12**, since carbon dioxide is reduced on the cathode electrode **12** and water is oxidized on the anode electrode **13** by using the methanol generation device. As shown in FIG. **1**A-FIG. **1**C, the amount of the reaction current can be monitored using the current measurement device **16**.

EXAMPLES

[0046] Hereinafter, the present disclosure will be described with reference to the following examples.

Inventive Example 1

Fabrication of the Cathode Electrode

[0047] A cathode electrode formed of CuNiAu according to the inventive example 1 was fabricated below.

[0048] First, Ni and Au were dissolved in Cu by a vacuum melting method so that x and y were respectively equal to 0.0558 and 0.0167. Subsequently, the dissolved material was solidified. In this way, CuNiAu was obtained. The obtained CuNiAu was shaped into a plate having a length of 20 millimeters, a width of 20 millimeters, and a thickness of 2 millimeters. The surface of the plate was washed using an organic solvent.

[0049] The composition of the CuNiAu plate was confirmed using an X-ray diffractometer. As a result, no peak of Au in the state of the elementary substance was observed. The formation of CuNiAu in which Au and Ni were dissolved in Cu was observed.

[0050] And then, the obtained CuNiAu plate was adhered to a glass substrate. In this way, the cathode electrode according to the inventive example 1 was fabricated.

Assembling of the Device

[0051] The methanol generation device shown in FIG. **1**C was fabricated using the above-mentioned cathode electrode. The elements of the methanol generation device are described below.

[0052] Cathode electrode: CuNiAu (Composition formula: $Cu_{0.9275}Ni_{0.0558}Au_{0.0167}$)

[0053] Anode electrode: Platinum

[0054] Electrode interval: approximately 8 centimeters

[0055] Reference electrode: Ag/AgCl

[0056] Anode-side electrolyte solution: potassium hydrogen carbonate aqueous solution having a concentration of 0.5 mol/L

[0057] Cathode-side electrolyte solution: potassium chloride aqueous solution having a concentration of 0.5 mol/L

[0058] Solid electrolyte membrane: Nafion membrane (available from Du Pont, Trade name: Nafion 117)

[0059] Carbon dioxide was supplied through a tube to the cathode-side electrolyte solution by bubbling the cathode-side electrolyte solution using a carbon dioxide gas for thirty minutes (carbon dioxide flow rate: 200 milliliters/minute).

Reduction of Carbon Dioxide

[0060] After carbon dioxide was dissolved in the cathode-side electrolyte solution, the container was sealed. Subsequently, a voltage was applied using a potentiostat so that the potential of the cathode electrode was negative with respect to the potential of the anode electrode. The value of the applied voltage was controlled using the potentiostat so that the potential of the cathode electrode with respect to the potential of the reference electrode was −1.9 volts.

[0061] After the voltage was applied for a certain period, the material and amount of the reaction products generated in the container were determined using gas chromatography and liquid chromatography. As a result, carbon monoxide (CO), formic acid (HCOOH), methane (CH_4), ethylene (C_2H_4), aldehydes, and ethanol were detected as reduction products of carbon dioxide. Furthermore, as shown in FIG. **2**, a peak was observed at the detecting position indicating the generation of methanol (i.e. the position indicated by the arrow depicted in the drawing) in the product analysis of the head-space gas chromatography. In other words, it was confirmed that methanol was generated using the cathode electrode formed of CuNiAu.

[0062] In the inventive example 1, the production amount of methanol per 1000 seconds of the electrolysis period was 2.2×10^{-7} mol/cm^2. Note that the electrolysis period was equal to the period for which the voltage was applied to the cathode electrode using the external power supply.

[0063] The faraday efficiency of the methanol generation in the inventive example 1 was calculated. As a result, the calculated faraday efficiency was 1.00%. Note that the faraday efficiency means a ratio of the charge amount used for the generation of the reaction product to the charge amount used for all the reactions. The faraday efficiency is calculated in accordance with the following formula:

(Faraday efficiency of the methanol generation)=(the charge amount used for the generation of methanol)/(the charge amount used for all the reactions)×100 [%].

Comparative Example 1

[0064] An experiment similar to that of the inventive example 1 was performed, except that a $Cu_{0.9442}Ni_{0.0558}$ electrode containing no Au was used as the cathode electrode.

[0065] As a result, CO, HCOOH, CH_4, C_2H_4, aldehydes, and ethanol were detected similarly to the inventive example 1. However, as shown in FIG. **2**, no signal was found at the detecting position of the methanol generation. In other words, methanol was not generated in the comparative example 1.

Comparative Example 2

[0066] An experiment similar to that of the inventive example 1 was performed, except that an Au electrode containing neither Cu nor Ni was used as the cathode electrode.

[0067] As a result, CO and HCOOH were detected. However, as shown in FIG. **2**, no signal was found at the detecting position of the methanol generation. In other words, methanol was not generated in the comparative example 2.

Comparative Example 3

[0068] An experiment similar to that of the inventive example 1 was performed, except that a Cu electrode containing neither Ni nor Au was used as the cathode electrode.

[0069] As a result, CO, HCOOH, CH_4, C_2H_4, aldehydes, and ethanol were detected similarly to the inventive example **1**. However, as shown in FIG. **2**, no signal was found at the detecting position of the methanol generation. In other words, methanol was not generated in the comparative example 3.

[0070] As just described, only in the case where the CuNiAu electrode was used, the generation of methanol was confirmed, as shown in FIG. **2**. In other words, the present inventors believe that a special effect which causes methanol to be generated occurs only in the case where the CuNiAu electrode formed of an alloy of Cu, Ni and Au is used, and that such a special effect does not occur in the case where the CuNi electrode, the Cu electrode, or the Au electrode is used.

Inventive Example 2

[0071] An experiment similar to that of the inventive example 1 was performed, except that a sodium chloride aqueous solution having a concentration of 0.5 mol/L was used as the cathode-side electrolyte solution.

[0072] As a result, it was confirmed that methanol was generated as the reduction product of carbon dioxide.

Inventive Example 3

[0073] An experiment similar to that of the inventive example 1 was performed, except that an electrode was used in which CuNiAu fine particles having a similar composition ratio to CuNiAu of the inventive example 1 were supported on a surface of a glassy carbon substrate.

[0074] As a result, it was confirmed that the obtained reaction products were almost the same as those of the inventive example 1 and that methanol was generated. Similar results were obtained in the case of using an electrode in which a CuNiAu thin film having a similar composition ratio to that of the inventive example 1 was laminated on the glassy carbon.

Inventive Example 4

[0075] An experiment similar to that of the inventive example 1 was performed, except that a CuNiAu electrode formed of $Cu_{0.795}Ni_{0.200}Au_{0.005}$ was used as the cathode electrode.

[0076] As a result, it was confirmed that methanol was generated as the reduction product of carbon dioxide.

Inventive Example 5

[0077] An experiment similar to that of the inventive example 1 was performed, except that a CuNiAu electrode formed of $Cu_{0.75}Ni_{0.20}Ah_{0.05}$ was used as the cathode electrode.

[0078] As a result, it was confirmed that methanol was generated as the reduction product of carbon dioxide.

Inventive Example 6

[0079] An experiment similar to that of the inventive example 1 was performed, except that the potentiostat was controlled so that the potential of the cathode electrode with respect to the potential of the reference electrode was −1.7 volts.

[0080] As a result, it was confirmed that methanol was generated as the reduction product of carbon dioxide.

Inventive Example 7

[0081] An experiment similar to that of the inventive example 1 was performed, except that the potentiostat was controlled so that the potential of the cathode electrode with respect to the potential of the reference electrode was **−2.1** volts.

[0082] As a result, it was confirmed that methanol was generated as the reduction product of carbon dioxide.

[0083] Table **1** shows the comparison of the methanol generation amounts obtained in the inventive examples 1-7 and the comparative examples 1-3. In Table 1, the generation amount of methanol generated in the inventive example 1 is set to be 100%. Each of the generation amounts of methanol generated in the inventive examples 2-7 and the comparative examples 1-3 is indicated relatively.

TABLE 1

	Methanol generation amount (relative amount, per unit charge amount)
Inventive example 1	100
Inventive example 2	96
Inventive example 3	89
Inventive example 4	39
Inventive example 5	67
Inventive example 6	80
Inventive example 7	95
Comparative example 1	0.0
Comparative example 2	0.0
Comparative example 3	0.0

[0084] As shown in Table 1, it was confirmed that methanol was generated in the inventive examples 1-7 and that methanol was not generated in the comparative examples 1-3.

[0085] As just described, it was confirmed that methanol was generated efficiently as the reduction product of carbon dioxide on the cathode electrode by using the cathode electrode having a region of CuNiAu.

[0086] While the present invention has been described with respect to preferred embodiments thereof, it will be apparent to those skilled in the art that the disclosed invention may be modified in numerous ways and may assume many embodiments other than those specifically described above. Accordingly, it is intended by the appended claims to cover all modifications of the invention that fall within the true spirit and scope of the invention.

INDUSTRIAL APPLICABILITY

[0087] The present disclosure provides a novel device and a novel method for generating methanol as the reduction product of carbon dioxide by using the cathode electrode having CuNiAu.

REFERENCE SIGNS LIST

[0088] **10**, **100**, **200** methanol generation device

[0089] **11** container

[0090] **12** cathode electrode

[0091] **13** anode electrode

[0092] **14** external power supply

[0093] **15** voltage measurement device

[0094] **16** current measurement device

[0095] **17**, **17**L, **17**R electrolyte solution

[0096] **18** tube

[0097] **19** solid electrolyte membrane

[0098] **20** reference electrode

1. A methanol generation device for generating methanol by reducing carbon dioxide, comprising:

a container for storing an electrolyte solution containing carbon dioxide;

a cathode electrode disposed in the container so as to be in contact with the electrolyte solution;

an anode electrode disposed in the container so as to be in contact with the electrolyte solution; and

an external power supply for applying a voltage so that a potential of the cathode electrode is negative with respect to a potential of the anode electrode,

wherein

the cathode electrode includes a region of $Cu_{1-x-y}Ni_xAu_y$ ($0<x$, $0<y$, and $x+y<1$); and

the anode electrode includes a region of a metal or a metal compound.

2. The methanol generation device according to claim **1**, wherein

the $Cu_{1-x-y}Ni_xAu_y$ is a solid solution or intermetallic compound of Cu, Ni, and Au.

3. The methanol generation device according to claim **1**, wherein

the value of x is more than 0 and not more than 0.20; and

the value of y is not less than 0.005 and not more than 0.05.

4. The methanol generation device according to claim **1**, wherein

the anode electrode is formed of carbon, platinum, gold, silver, copper, titanium, iridium oxide, or an alloy thereof.

5. The methanol generation device according to claim **1**, wherein

the electrolyte solution is a potassium chloride aqueous solution or a sodium chloride aqueous solution.

6. The methanol generation device according to claim **1**, wherein

an absolute value of the voltage is not less than 2.5 volts.

7. The methanol generation device according to claim **1**, further comprising:

a reference electrode disposed in the container so as to be in contact with the electrolyte solution,

wherein

the reference electrode has a region of Ag/AgCl; and

the voltage to be applied by the external power supply to the cathode electrode with respect to a potential of the reference electrode is not more than −1.7 volts.

8. The methanol generation device according to claim **1**, further comprising:

a solid electrolyte membrane for dividing the container into a cathode container for storing a first electrolyte solution containing carbon dioxide and an anode container for storing a second electrolyte solution.

9. The methanol generation device according to claim **8**, wherein

the first electrolyte solution is a potassium chloride aqueous solution or a sodium chloride aqueous solution; and

the second electrolyte solution is a potassium hydrogen carbonate aqueous solution, a sodium hydrogen carbonate aqueous solution, or a potassium sulfate aqueous solution.

10. A method for generating methanol using a methanol generation device, the method comprising:

(a) preparing the methanol generation device comprising:

a container;

a cathode electrode; and

an anode electrode,

wherein

the cathode electrode includes a region of $Cu_{1-x-y}Ni_xAu_y$ ($0<x$, $0<y$, and $x+y<1$);

the anode electrode includes a region of a metal or a metal compound;

an electrolyte solution is stored in the container;

the cathode electrode is in contact with the electrolyte solution;

the anode electrode is in contact with the electrolyte solution; and

the electrolyte solution contains carbon dioxide; and

(b) reducing the carbon dioxide contained in the electrolyte solution by applying a voltage so that a potential of the cathode electrode is negative with respect to a potential of the anode electrode to generate methanol on the cathode electrode.

11. The method according to claim **10**, wherein

the methanol generation device is placed under room temperature and atmospheric pressure in step (b).

12. An electrode for generating methanol used for a methanol generation device for generating methanol by reducing carbon dioxide, comprising:

a region of $Cu_{1-x-y}Ni_xAu_y$ ($0<x$, $0<y$, and $x+y<1$).

* * * * *