**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 the 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}Ni_{x}Au_{y} (0<x, 0<y, and x+y<1). The anode electrode has a region of a metal or a metal compound.
METHANOL GENERATION DEVICE, METHOD FOR GENERATING METHANOL, AND ELECTRODE FOR GENERATING METHANOL

CROSS REFERENCE TO RELATED APPLICATIONS


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


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_{x}Au_{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. 1A shows a schematic view of a methanol generation device according to the present disclosure.

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

[0020] FIG. 1C 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. 1A-FIG. 1C 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. 1A, 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 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_{x}Au_{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_{x}Au_{y} represents the composition ratio of Ni to CuNiAu. The value of y in the composition formula Cu_{1-x-y},Ni_{x}Au_{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
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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. 1A, 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. 1B, 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 17L and a cathode-side electrolyte solution 17R. 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 17L and a cathode container for storing the cathode-side electrolyte solution 17R.

0037. The solid electrolyte membrane 19 prevents the anode-side electrolyte solution 17L and the cathode-side electrolyte solution 17R 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 17R with the anode-side electrolyte solution 17L 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. 1C, 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 17R. 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 oxidation 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. 1A or FIG. 1B, 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. 1C, 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 oxidation 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. 1B and FIG. 1C, the cathode-side electrolyte solution 17R and the anode-side electrolyte solution 17L 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. 1A-FIG. 1C, 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. 1C 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_{0.9272}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 (CH₄), ethylene (C₂H₄), 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 2.2x10⁻⁷ mol/cm². 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:

\[(\text{Faraday efficiency of the methanol generation}) \times (\text{the charge amount used for the generation of methanol}) \times (\text{the charge amount used for all the reactions}) \times 100 \%\]

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, CH₄, C₂H₄, 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.
As a result, CO, HCOOH, CH₄, C₂H₄, 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.

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

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.

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

Inventive Example 3

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.

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

An experiment similar to that of the inventive example 1 was performed, except that a CuNiAu electrode formed of Cu₀.₇₅Ni₀.₂₀Au₀.₀₅ was used as the cathode electrode.

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

Inventive Example 5

An experiment similar to that of the inventive example 1 was performed, except that a CuNiAu electrode formed of Cu₀.₇₅Ni₀.₂₀Au₀.₀₅ was used as the cathode electrode.

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

Inventive Example 6

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.

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

Inventive Example 7

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.

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

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>
<thead>
<tr>
<th>TABLE 1</th>
<th>Methanol generation amount (relative amount, per unit charge amount)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inventive example 1</td>
<td>100</td>
</tr>
<tr>
<td>Inventive example 2</td>
<td>96</td>
</tr>
<tr>
<td>Inventive example 3</td>
<td>89</td>
</tr>
<tr>
<td>Inventive example 4</td>
<td>39</td>
</tr>
<tr>
<td>Inventive example 5</td>
<td>67</td>
</tr>
<tr>
<td>Inventive example 6</td>
<td>80</td>
</tr>
<tr>
<td>Inventive example 7</td>
<td>95</td>
</tr>
<tr>
<td>Comparative example 1</td>
<td>0.0</td>
</tr>
<tr>
<td>Comparative example 2</td>
<td>0.0</td>
</tr>
<tr>
<td>Comparative example 3</td>
<td>0.0</td>
</tr>
</tbody>
</table>

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.

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.

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

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

10, 100, 200 methanol generation device
11 container
12 cathode electrode
13 anode electrode
14 external power supply
15 voltage measurement device
16 current measurement device
17, 17L, 17R electrolyte solution
18 tube
19 solid electrolyte membrane
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$_{1-x}$Ni$_x$Au$_y$ (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$_{1-x}$Ni$_x$Au$_y$ 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$_{1-x}$Ni$_x$Au$_y$ (0<x, 0<y, and x+y<1); and
        the anode electrode includes a region of a metal or a metal compound;
    (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.