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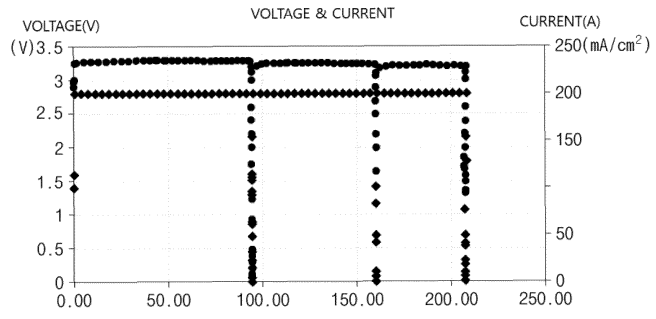
(54) ELECTROLYSIS DEVICE AND OPERATION METHOD THEREFOR

(57) The present disclosure relates to an electrolysis device including an electrolysis stack in which one or more electrolysis cells including an anode, a cathode, a separator, and an electrolyte solution are stacked, an anode inlet connected to the anode to transfer the electrolyte solution, and a cathode outlet connected to the cathode to discharge a product and an unreacted reactant from the cathode, wherein in the cathode outlet, a back pressure is applied to the product and the unreacted reactant discharged from the cathode outlet.

[FIG. 1]



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Description

TECHNICAL FIELD

Cross-reference to Related Application

[0001] This application claims the benefit of Korean Patent Application No. 10-2022-0128363, filed on October 7, 2022, in the Korean Intellectual Property Office, the disclosure of which is incorporated herein in its entirety by reference.

Technical Field

[0002] The present invention relates to an electrolysis device for electrolyzing carbon dioxide and a method for operating the device.

BACKGROUND ART

[0003] Carbon dioxide is a greenhouse gas that causes global warming, and thus, should be reduced. As a method for reducing carbon dioxide, methods such as capture, chemical conversion, or electrochemical conversion are known. Among the above-described methods, the electrochemical conversion method allows for a precise control of components so as to produce other synthetic gases, which is more economically beneficial than simply removing carbon dioxide. In addition, carbon dioxide may be electrolyzed together with water to obtain carbon monoxide, ethylene, methane, formic acid, formate, various hydrocarbons, and an organic substance such as an aldehyde or an alcohol.

[0004] A process of electrochemically decomposing carbon dioxide is similar to a technique of electrolyzing water. However, since the activity of an electrochemical reaction improves in a strong base atmosphere, an aqueous KOH solution of a certain concentration is generally used as an electrolyte solution. When a current is applied while supplying water to an anode, the water is decomposed into a hydrogen ion and an electron together with the generation of oxygen gas. The electron is transferred to a cathode through an external conductive line, and the hydrogen ion is transferred to the cathode through an ion-selective separator. At this time, the transferred electron reacts with carbon dioxide and water supplied to the cathode and then is decomposed into carbon monoxide and a hydroxide ion (OH^-), and the generated hydroxide ion reacts with a hydrogen ion (H^+) of an anode to produce water, thereby being in an electrical neutral state. Through the above process, an electrochemical decomposition reaction of carbon dioxide is completed. At this time, the water supplied together with the carbon dioxide reacts with the transferred electron, which is separate from the carbon monoxide production reaction, and is electrolyzed, thereby producing hydrogen gas, and at the same time, producing a hydroxide ion. Such a reaction of water and an electron may be said to have a competitive relationship with the carbon monoxide production reaction. Since the reactions are electrochemical reactions, the generation amount of carbon monoxide and a ratio of hydrogen/carbon dioxide may be easily controlled by controlling a voltage.

[0005] In a process of electrolyzing carbon dioxide using an electrolysis device, in order to improve the conversion rate of carbon dioxide, a method for increasing the flow and flow speed of supplied carbon dioxide has been typically used. In this case, since the amount of supplied carbon dioxide increases, the conversion rate of carbon dioxide may improve for a predetermined operation time. However, the amount of unreacted carbon dioxide which is not electrolyzed inside the electrolysis device and escapes to the outside, and then is circulated back to the electrolysis device increases, which eventually leads to a situation in which excessive current and voltage are applied, and as a result, there is a limitation in that it is not efficient in terms of the rate of use of carbon dioxide.

[0006] In addition, as the active area of a cell or stack included in an electrolysis device increases, there is a case in which gases and liquids penetrate through a separator and are mixed, and in this case, a salt is produced and the like, which degrade electrolysis efficiency.

(Patent Document 001) JP 2022-042280 A

DISCLOSURE OF THE INVENTION

TECHNICAL PROBLEM

[0007] An aspect of the present invention provides an electrolysis device, wherein a back pressure is applied to the inside of a cathode outlet of the electrolysis device to prevent a phenomenon in which an electrolyte solution flows from an anode to a cathode and to maintain electrolysis efficiency at an excellent level.

[0008] Another aspect of the present invention provides a method for operating an electrolysis device, wherein a back pressure is applied to the inside of a cathode outlet of the electrolysis device to reduce the flow rate of a product and

unreacted carbon dioxide to be discharged, thereby improving the rate of use of supplied carbon dioxide.

TECHNICAL SOLUTION

[0009] The present invention provides an electrolysis device and a method for operating the same.

(1) The present invention provides an electrolysis device including an electrolysis stack in which one or more electrolysis cells including an anode, a cathode, a separator, and an electrolyte solution are stacked, an anode inlet connected to the anode to transfer the electrolyte solution, and a cathode outlet connected to the cathode to discharge a product and an unreacted reactant from the cathode, wherein in the cathode outlet, a back pressure is applied to the product and the unreacted reactant discharged from the cathode outlet.
(2) In (1) above, the present invention provides an electrolysis device, wherein the back pressure is about 10 kPa to about 50 kPa.
(3) In (1) or (2) above, the present invention provides an electrolysis device, wherein the cathode outlet includes a pressure control valve.
(4) In any one of (1) to (3) above, the present invention provides an electrolysis device, wherein the electrolysis stack has an electrode area of about 500 cm^2 to about 5,000 cm^2.
(5) In any one of (1) to (4) above, the present invention provides an electrolysis device, wherein the electrolyte solution has a loss flow rate of about 0.1 L/day or less.
(6) In any one of (1) to (5) above, the present invention provides an electrolysis device, wherein the electrolysis cell is a membrane electrode assembly (MEA) having a zero-gap structure in which a gas diffusion layer, a cathode, a separator, and an anode with an electrolyte flow path are sequentially stacked.
(7) In any one of (1) to (6) above, the present invention provides an electrolysis device, wherein the electrolysis device electrolyzes carbon dioxide.
(8) In any one of (1) to (7) above, the present invention provides an electrolysis device, wherein the electrolysis device produces at least one selected from the group consisting of carbon monoxide, ethylene, methane, formic acid, hydrocarbon, aldehyde, and alcohol.
(9) The present invention provides a method for operating an electrolysis device, wherein the method includes supplying an electrolyte solution through an anode inlet to an electrolysis stack in which one or more electrolysis cells including an anode, a cathode, a separator, and an electrolyte solution are stacked, and supplying a reactant through a cathode inlet S1, performing an electrolysis reaction on the reactant in the electrolysis stack S2, and discharging a product produced by the electrolysis reaction of the step S2 and an unreacted reactant through a cathode outlet to the outside of the electrolysis stack S3, wherein in the step S3, a back pressure of about 10 kPa to about 50 kPa is applied to the product and the unreacted reactant discharged through the cathode outlet.
(10) In (9) above, the present invention provides a method for operating an electrolysis device, wherein the back pressure in the step S3 is about 20 kPa to about 40 kPa.
(11) In (9) or (10) above, the present invention provides a method for operating an electrolysis device, wherein in the step S1, the supply flow rate of the reactant is maintained constant while the electrolysis reaction is performed.
(12) In any one of (9) to (11) above, the present invention provides a method for operating an electrolysis device, wherein the back pressure is controlled by opening and closing of a pressure control valve disposed in the cathode outlet.
(13) In any one of (9) to (12) above, the present invention provides a method for operating an electrolysis device, wherein the unreacted reactant discharged in the step S3 are circulated back into the electrolysis stack.

ADVANTAGEOUS EFFECTS

[0010] According to an electrolysis device of the present invention, a back pressure is applied to a cathode outlet to prevent a phenomenon in which an electrolyte solution flows from an anode to a cathode when an electrochemical reaction is performed, and as a result, electrolysis efficiency and overvoltage may be maintained at an excellent level.

[0011] According to a method for operating an electrolysis device of the present invention, the amount of carbon dioxide used in an electrochemical reaction may be increased even if the same carbon dioxide is supplied, so that the conversion rate of carbon dioxide and the Faraday efficiency of carbon monoxide may be increased, and the consumption of power for recirculating unreacted carbon dioxide may be reduced.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]

FIG. 1 is a graph of voltage and current data of a long-term performance evaluation of Example 5.
FIG. 2 is a graph of carbon dioxide and hydrogen Faraday efficiency data of the long-term performance evaluation of Example 5.
FIG. 3 is a graph of voltage and current data of a long-term performance evaluation of Comparative Example 5.

MODE FOR CARRYING OUT THE INVENTION

[0013] Hereinafter, the present invention will be described in more detail to facilitate understanding of the present invention. In this case, it will be understood that words or terms used in the specification and claims shall not be interpreted as having the meaning defined in commonly used dictionaries. It will be further understood that the words or terms should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and the technical idea of the invention, based on the principle that an inventor may properly define the meaning of the words or terms to best explain the invention.

[0014] The terms used herein are only used to describe exemplary embodiments, and are not intended to limit the present invention. The terms of a singular form may include plural forms unless the context clearly indicates otherwise.

[0015] In the present specification, it should be understood that the terms ,"include," "comprise," or "have" are intended to specify the presence of stated features, numbers, steps, elements, or combinations thereof, but do not preclude the presence or addition of one or more other features, numbers, steps, elements, or combinations thereof.

Method for operating electrolysis device

[0016] A method for operating an electrolysis device of the present invention includes supplying an electrolyte solution through an anode inlet to an electrolysis stack in which one or more electrolysis cells including an anode, a cathode, a separator, and an electrolyte solution are stacked, and supplying a reactant through a cathode inlet S1, performing an electrolysis reaction on the reactant in the electrolysis stack S2, and discharging a product produced by the electrolysis reaction of the step S2 and an unreacted reactant through a cathode outlet to the outside of the electrolysis stack S3, wherein in the step S3, a back pressure of about 10 kPa to about 50 kPa is applied to the product and the unreacted reactant discharged through the cathode outlet.

[0017] The electrolysis device of the present invention may include an electrolysis cell or an electrolysis stack in which two or more electrolysis cells are stacked, a cathode inlet, a cathode outlet, an anode inlet, and an anode outlet. As to be described later, the electrolysis cell may include an anode, a cathode, a separator disposed between the anode and the cathode, and an electrolyte solution. In addition, in order to increase a driving voltage and current efficiency, the electrolysis cell may form a membrane electrode assembly having a zero-gap structure in which a gas diffusion layer, a cathode, a separator, and an anode with an electrolyte flow path are sequentially stacked, and in this case, separator plates may be disposed on both sides of the membrane electrode assembly to form one cell.

[0018] The cathode inlet may serve to supply reactants to the electrolysis cell, and may be disposed adjacent to the cathode. In addition, the cathode outlet may serve to discharge products produced by an electrochemical reaction and unreacted reactants from the electrolysis cell to the outside, and may be disposed adjacent to the cathode. In addition, the anode inlet may serve to supply the electrolyte solution into the electrolysis cell or stack, and the anode outlet may serve to discharge the used electrolyte solution to the outside after the electrolysis reaction.

[0019] Meanwhile, in a typical method for electrolyzing carbon dioxide, in order to obtain a high conversion rate, a method for supplying carbon dioxide, which is a reactant, to an electrolysis cell by increasing the flow rate and flow speed of the carbon dioxide is used, while operating an electrolysis device under the atmospheric pressure condition. In this case, the conversion rate may be increased by increasing the amount of introduced carbon dioxide, but the amount of carbon dioxide unreacted inside the electrolysis cell and discharged again increases, and the unreacted carbon dioxide is required to be circulated again and introduced into the electrolysis cell, so that the consumption of current and power used for circulating the carbon dioxide is significant. In addition, the greater the amount of the unreacted carbon dioxide, the greater the cost and time consumed in a process of classifying the unreacted carbon dioxide and a product discharged theretogether.

[0020] In addition, in a typical method for electrolyzing carbon dioxide, if the active area of an electrolysis cell or stack increases to 1000 cm^2 or greater, there may be a problem in that gases or liquids penetrate through pores of a separator and are mixed. Specifically, an unreacted carbon dioxide gas supplied from the cathode flows to the anode, and the electrolyte solution flows from the anode to the cathode, resulting in the generation of a salt, which may cause a problem in which electrolysis efficiency is degraded and continuous operation is not possible.

[0021] The method for operating an electrolysis device of the present invention maintains the flow rate and flow speed of supplied carbon dioxide constant during the electrolysis reaction, but reduces the flow rate of a product and unreacted carbon dioxide discharged from the cathode outlet, thereby allowing sufficiently more carbon dioxide to react inside the electrolysis cell. That is, the method for operating an electrolysis device of the present invention may pressurize the inside

of the cathode outlet to increase the pressure inside the electrolysis cell and/or stack, thereby increasing the amount of reacted carbon dioxide, and accordingly, the rate of use of carbon dioxide and the Faraday efficiency of carbon monoxide may be improved. In addition, even in the case of an electrolysis cell or stack having an active area of about 1000 cm^2 or greater, by applying a back pressure to the inside of a cathode outlet, thereby controlling an internal pressure ratio between the cathode outlet and an anode inlet, it is possible to prevent a phenomenon in which an electrolyte solution transfers a salt through a separator, or an unreacted carbon dioxide gas flows over.

[0022] According to an embodiment of the present invention, the method for operating an electrolysis device of the present invention may be performed through supplying carbon dioxide to the electrolysis device S1, electrolyzing the carbon dioxide S2, and discharging a product produced by electrolyzing the carbon dioxide and unreacted carbon dioxide S3, wherein the discharging of the product and the unreacted carbon dioxide of the step S3 may be performed by applying a back pressure to the product and the unreacted reactant to be discharged.

[0023] The back pressure refers to a resistive pressure acting in a direction opposite to a direction in which a fluid flows when the fluid is discharged through a tube. A cathode outlet of the present invention may include a pressure control valve to be described below, wherein the back pressure may be controlled by changing a width of the cathode outlet through the opening and closing of the pressure control valve, and a pressure may be applied in a direction opposite to a direction in which a product and an unreacted reactant to be discharged through the cathode outlet are discharged.

[0024] According to an embodiment of the present invention, in the step S3, a back pressure of about 10 kPa to about 50 kPa may be applied to the product and the unreacted reactant discharged through the cathode outlet. Specifically, the back pressure may be about 10 kPa or greater, about 13 kPa or greater, about 15 kPa or greater, about 17 kPa or greater, about 20 kPa or greater, about 22 kPa or greater, about 25 kPa or greater, about 27 kPa or greater, about 32 kPa or greater, about 50 kPa or less, about 47 kPa or less, about 45 kPa or less, about 42 kPa or less, about 40 kPa or less, about 37 kPa or less, about 35 kPa or less, about 32 kPa or less, or about 30 kPa or less. If the back pressure is out of the lower limit of the above-described pressure value range, a pressure applied to a product and an unreacted reactant to be discharged is low, resulting in a small amount of reduction in the flow rate of the product and the unreacted reactant to be discharged, so that it is difficult to expect an improvement in the rate of use of carbon dioxide and the Faraday efficiency of carbon monoxide. In addition, if the back pressure is out of the upper limit of the above-described pressure value range, a pressure applied to a product and an unreacted reactant to be discharged is high, resulting in a reduced amount of a product reacted inside the electrolysis cell, and the conversion rate of carbon dioxide may be decreased, and the overvoltage may be increased.

[0025] In addition, according to an embodiment of the present invention, an internal pressure of the cathode outlet and an internal pressure of the anode inlet may be controlled to satisfy Equation 1 below.

[Equation 1]

$$P_{cathode\_out} / P_{anode\_in} \geq 1$$

[0026] In Equation 1 above,

$P_{cathode\_out}$ is the internal pressure of the cathode outlet, and
P_{anode_in} is the internal pressure of the anode inlet.

[0027] Specifically, if the internal pressure of a cathode outlet is equal to or higher than the internal pressure of an anode inlet, the loss of an electrolyte solution is reduced to about 0.1 L/day or less, and an electrolysis device may be continuously operated without degradation in electrolysis efficiency. However, if the internal pressure of a cathode outlet is less than the internal pressure of an anode inlet, an electrolyte solution penetrates a separator and is transferred to the cathode outlet, and the loss of an electrolyte solution corresponds to a level of about 0.5 L/h, making it difficult to drive an electrolysis device continuously.

[0028] According to an embodiment of the present invention, the electrolyte solution may have a loss flow rate of about 0.1 L/day or less. For example, the loss flow rate of the electrolyte solution may be about 0.1 L/day or less, about 0.09 L/day or less, about 0.08 L/day or less, about 0.07 L/day or less, about 0.06 L/day or less, about 0.05 L/day or less, about 0.04 L/day or less, about 0.03 L/day or less, about 0.02 L/day or less, or about 0.01 L/day or less. On the other hand, in the case of a typical electrolysis device in which a back pressure is not applied to a cathode outlet, the loss flow rate corresponds to a level of about 0.5 L/h or greater, and in this case, an amount of a salt generated by an electrolysis solution flowing to a cathode through a separator increases, so that a continuous electrical conversion reaction is impossible.

[0029] Here, the loss flow rate of the electrolyte solution is measured by an amount of the electrolyte solution lost over time with respect to an initial amount of the electrolyte solution contained inside the electrolysis cell.

[0030] According to an embodiment of the present invention, in the step S1, the supply flow rate of the reactant may be maintained constant during an electrolysis reaction. The method for operating an electrolysis device of the present

invention maintains the supply flow rate and flow speed of carbon dioxide supplied to an electrolysis cell constant, but controls the discharge flow rate of a product and unreacted carbon dioxide discharged, so that the rate of use of carbon dioxide may be increased. The method for operating an electrolysis device of the present invention may solve a limitation, the limitation which may occur when a supply flow rate and a flow rate are typically increased, in which the rate of use of carbon dioxide is decreased, and the amount of unreacted carbon dioxide recirculated into the electrolysis cell is increased.

[0031] According to an embodiment of the present invention, the unreacted reactant discharged in the step S3 may be circulated back into the electrolysis cell. The method for operating an electrolysis device of the present invention may reduce an amount of unreacted carbon dioxide by increasing the rate of use of carbon dioxide, and thus, may reduce the consumption of power which may be used for circulating the unreacted carbon dioxide back into the electrolysis cell. In addition, the method for operating an electrolysis device of the present invention may increase the Faraday efficiency of carbon monoxide to reduce the consumption of a driving current applied to an electrolysis device.

[0032] According to an embodiment of the present invention, the cathode outlet includes a pressure control valve, and a pressure on the product and the unreacted reactant may be controlled by opening and closing the pressure control valve. Specifically, the cathode outlet of the electrolysis device of the present invention may include a pressure control valve, and a pressure inside the cathode outlet may be controlled by opening or closing the pressure control valve. The pressure inside the cathode outlet may be increased by closing the pressure control valve, and the flow rate may be decreased by applying a pressure to the product and the unreacted carbon dioxide.

[0033] According to an embodiment of the present invention, the electrolysis cell includes a cathode, an anode and a separator, wherein the separator may be a porous separator, and particularly, may be a porous separator having hydrophilic properties. Specifically, the porous separator may be an ion-selective exchange membrane, and the porous separator may include an anion exchange membrane, a cation exchange membrane, or an amphoteric ion exchange membrane. In addition, the porous separator may include a hydrophilic porous substrate, and thus, may allow a moisture content to be maintained at a certain level. In addition, the porous separator includes a porous substrate including pores having an average particle diameter of about 10 nm to about 750 nm, and thus, may provide a path for allowing various molecules including ions and water molecules to be smoothly transferred by an aqueous solution-based electrolyte, and accordingly, the carbon dioxide conversion rate may be increased, and the overvoltage may be reduced during the operation of the electrolysis device.

[0034] The hydrophilic porous substrate may be a cellulose-based resin. Specifically, the hydrophilic porous substrate may be a cellulose-based resin, and the cellulose-based resin may be one or more selected from the group consisting of cellulose acetate, cellulose triacetate, cellulose propionate, cellulose butyrate, cellulose acetylpropionate, cellulose diacetate, cellulose dibutyrate, cellulose tributyrate, and cellulose nitrate. More specifically, the porous substrate contained in the porous separator included in the electrolysis cell of the present invention may include cellulose acetate.

[0035] Particularly, the cellulose acetate has hydrophilic properties, has high mechanical and chemical strength due to high dimensional limitation which does not allow dimensions and shapes to be changed under conditions such as temperature or humidity, and has a uniform pore structure. Meanwhile, in a porous separator used in an electrolysis cell for converting carbon dioxide, pores formed in the porous separator are impregnated with an aqueous solution-based electrolyte solution, and ions such as HCO_3^-, CO_3^{2-}, and OH^- may be transferred through the pores. Accordingly, when cellulose acetate having the hydrophilic properties, high mechanical strength, and an uniform pore size is used as a separator of a carbon dioxide electrolysis cell using an aqueous solution-based electrolyte solution, properties of a high carbon dioxide conversion rate, high Faraday efficiency of carbon monoxide, and a low overvoltage may be exhibited.

[0036] In addition, the method for operating an electrolysis device of the present invention uses a large-area electrolysis unit cell of about 100 cm^2 or greater including the above-described porous separator, and thus, may be applied to a high-performance unit cell or a stack in which a plurality of unit cells are stacked.

Electrolysis device

[0037] The electrolysis device of the present invention includes an electrolysis stack in which one or more electrolysis cells including an anode, a cathode, a separator, and an electrolyte solution are stacked, an anode inlet connected to the anode to transfer the electrolyte solution, and a cathode outlet connected to the cathode to discharge a product and an unreacted reactant from the cathode, wherein in the cathode outlet, a back pressure is applied to the product and the unreacted reactant discharged from the cathode outlet. Specifically, the electrolysis device of the present invention may include an electrolysis cell or an electrolysis stack in which two or more electrolysis cells are stacked, a cathode inlet, a cathode outlet, an anode inlet, and an anode outlet. In addition, the electrolysis cell may include an anode, a cathode, a separator disposed between the anode and the cathode, and an electrolyte solution, and in order to increase a driving voltage and current efficiency, the electrolysis cell may form a membrane electrode assembly having a zero-gap structure in which a gas diffusion layer, a cathode, a separator, and an anode with an electrolyte flow path are sequentially stacked, and in this case, separator plates may be disposed on both sides of the membrane electrode assembly to form one cell. In

addition, the electrolysis device of the present invention is the same as described in the method for operating an electrolysis device of the present specification.

[0038] The back pressure is about 10 kPa to about 50 kPa, and is the same as described in the method for operating an electrolysis device of the present specification. Additionally, if the above back pressure range is satisfied and an internal pressure of the cathode outlet is equal to or higher than an internal pressure of the anode inlet, the loss of the anode transferred from the anode to the cathode is reduced, and the electrolysis device may be continuously operated with high efficiency.

[0039] The internal pressure of the cathode outlet of the electrolysis device may be about 10 kPa to about 300 kPa, and the internal pressure of the anode outlet may be about 5 kPa to about 60 kPa. For example, the internal pressure of the cathode outlet of the electrolysis device may be about 10 kPa or greater, about 30 kPa or greater, about 50 kPa or greater, about 60 kPa or greater, about 70 kPa or greater, about 90 kPa or greater, about 100 kPa or greater, about 110 kPa or greater, about 120 kPa or greater, about 130 kPa or greater, about 300 kPa or less, about 270 kPa or less, about 230 kPa or less, about 220 kPa or less, about 210 kPa or less, about 200 kPa or less, about 190 kPa or less, about 170 kPa or less, about 160 kPa or less, about 150 kPa or less, or about 140 kPa or less. In addition, for example, the internal pressure of the anode outlet may be about 5 kPa or greater, about 7 kPa or greater, about 9 kPa or greater, about 10 kPa or greater, about 12 kPa or greater, about 15 kPa or greater, about 20 kPa or greater, about 22 kPa or greater, about 25 kPa or greater, about 27 kPa or greater, about 30 kPa or greater, about 60 kPa or less, about 57 kPa or less, about 55 kPa or less, about 53 kPa or less, about 50 kPa or less, about 48 kPa or less, about 45 kPa or less, about 42 kPa or less, about 40 kPa or less, about 39 kPa or less, about 37 kPa or less, or about 35 kPa or less.

[0040] The cathode outlet may include a pressure control valve, wherein the back pressure may be controlled through the pressure control valve, and the contents related to the pressure control valve and the back pressure control are the same as described in the method for operating an electrolysis device of the present specification.

[0041] In addition, according to an embodiment of the present invention, an internal pressure of the cathode outlet and an internal pressure of the anode inlet may be controlled to satisfy Equation 1 below.

[Equation 1]

$$P_{cathode\_out} / P_{anode\_in} \geq 1$$

[0042] In Equation 1 above,

$P_{cathode\_out}$ is the internal pressure of the cathode outlet, and
P_{anode_in} is the internal pressure of the anode inlet.

[0043] Specifically, if the internal pressure of a cathode outlet is equal to or higher than the internal pressure of an anode inlet, the loss of an electrolyte solution is reduced to about 0.1 L/day or less, and an electrolysis device may be continuously operated without degradation in electrolysis efficiency. However, if the internal pressure of a cathode outlet is less than the internal pressure of an anode inlet, an electrolyte solution penetrates a separator and is transferred to the cathode outlet, and the loss of an electrolyte solution corresponds to a level of about 0.5 L/h, making it difficult to drive an electrolysis device continuously.

[0044] According to an embodiment of the present invention, the electrolyte solution may have a loss flow rate of about 0.1 L/day or less. For example, the loss flow rate of the electrolyte solution may be about 0.1 L/day or less, about 0.09 L/day or less, about 0.08 L/day or less, about 0.07 L/day or less, about 0.06 L/day or less, about 0.05 L/day or less, about 0.04 L/day or less, about 0.03 L/day or less, about 0.02 L/day or less, or about 0.01 L/day or less. On the other hand, in the case of a typical electrolysis device in which a back pressure is not applied to a cathode outlet, the loss flow rate corresponds to a level of about 0.5 L/h or greater, and in this case, an amount of a salt generated by an electrolysis solution flowing to a cathode through a separator increases, so that a continuous electrical conversion reaction is impossible.

[0045] Here, the loss flow rate of the electrolyte solution is measured by an amount of the electrolyte solution lost over time with respect to an initial amount of the electrolyte solution contained inside the electrolysis cell.

[0046] FIG. 1 is a graph of voltage and current data of a long-term performance evaluation of Example 5, FIG. 2 is a graph of carbon dioxide and hydrogen Faraday efficiency data of the long-term performance evaluation of Example 5, and FIG. 3 is a graph of voltage and current data of a long-term performance evaluation of Comparative Example 5.

[0047] Referring to FIG. 1 and FIG. 2, when a back pressure of about 0.3 bar and about 30 kPa is applied to a cathode outlet, salt generation is suppressed, thereby allowing a long term operation, an overvoltage is rather decreased, and a reaction current density of about 200 mA/cm^2 is maintained. In addition, the Faraday efficiency of carbon dioxide may be maintained at a high level, and the Faraday efficiency of hydrogen may not increase. On the other hand, referring to FIG. 3, if no back pressure is applied to the cathode outlet, the electrolyte solution flows over to the cathode side through the

separator, thereby generating a salt, and as a result, the overvoltage increases after about 12 hours of operation, and the reaction current is not maintained and decreases.

[0048] Meanwhile, in the case of a fuel cell, there is difficulty in forming the same into a large-area electrochemical cell or stack in consideration of the specifications when the cell or stack is actually used, but in the case of a cell or stack included in an electrolysis device, the cell or stack may be formed in a large area in order to increase the conversion amount of carbon dioxide or water per unit time. At this time, in the case of the electrolysis cell or stack, it is important to maintain the large area for a long period of time and at the same time to maintain physical/chemical durability and high electrolysis efficiency. However, as the electrode area of the cell or stack increases on a large scale, the area of an applied separator also increases, and accordingly, the supply flow rate of a reaction gas also increases, and when a large amount of reaction gas is supplied into the cell or stack, the internal pressure thereof also increases, so that a pressure gradient is created between an anode and a cathode based on the separator, causing a phenomenon in which materials of both electrodes are mixed with each other through the separator. Therefore, in the electrolysis device of the present invention, the pressure relationship between the cathode outlet and the anode inlet is controlled at a certain ratio even under the condition of such a large-scale cell or stack, resulting in the development of an electrolysis device which maintains long-term durability without the mixing of materials of both electrodes and has high electrolysis efficiency.

[0049] According to an embodiment of the present invention, the electrolysis stack may have an electrode area of about 500 cm^2 to about 5,000 cm^2. The electrode area of the electrolysis stack refers to an area in which an electrolysis reaction is activated, and the electrode area of such an electrolysis stack may be about 500 cm^2 to about 5,000 cm^2. For example, the electrolysis stack may have an electrode area of about 500 cm^2 or larger, about 600 cm^2 or larger, about 700 cm^2 or larger, about 800 cm^2 or larger, about 1,000 cm^2 or larger, about 1,200 cm^2 or larger, about 1,500 cm^2 or larger, about 2,000 cm^2 or larger, about 2,500 cm^2 or larger, about 5,000 cm^2 or smaller, about 4,500 cm^2 or smaller, about 4,300 cm^2 or smaller, about 4,100 cm^2 or smaller, about 4,000 cm^2 or smaller, about 3,800 cm^2 or smaller, about 3,500 cm^2 or smaller, about 3,300 cm^2 or smaller, about 3,100 cm^2 or smaller, about 3,000 cm^2 or smaller, specifically, about 1,000 cm^2 to about 4,000 cm^2. The electrolysis device of the present invention includes a cell or stack satisfying the above-described electrode area range, and thus, may maintain high electrolysis efficiency per unit time and high physical/chemical durability for a long period of time.

[0050] According to another embodiment of the present invention, the electrolysis device may be used in all of the field of electrochemical conversion, and the electrolysis device may be a fuel cell, a device capable of producing useful chemicals through electrochemical conversion such as water electrolysis, or a device which may be utilized for reducing and converting carbon dioxide and NOx. Specifically, the electrolysis device may be an electrochemical conversion device which converts carbon dioxide into carbon monoxide and ethylene.

[0051] According to an embodiment of the present invention, the electrolysis device may include a cell or stack which converts introduced carbon dioxide into carbon monoxide, and the cell or stack may include an anode, a cathode, an electrolyte, and a separator. In addition, the cell may be a membrane electrode assembly (MEA) having a zero-gap structure in which a gas diffusion layer, a cathode, a separator, and an anode with an electrolyte flow path are sequentially stacked.

[0052] The electrolysis refers to decomposing a material through a redox reaction by applying a direct current voltage to perform a decomposition reaction which does not occur spontaneously. The anode is an oxidation electrode which oxidizes water to generate oxygen, at which time, a hydrogen ion is generated. The hydrogen ion generated in the anode is transferred to the cathode through the electrolyte, and the cathode is a reduction electrode in which a reactant introduced into the cathode may react with an electron the hydrogen ions transferred from the anode and generate a product. In addition, the separator may be disposed between the anode and the cathode. The separator itself may be composed of an inert material that does not participate in an electrochemical reaction, but provides a path for allowing an ion to be transferred between the anode and the cathode, and may serve to separate a physical contact of the anode and the cathode.

[0053] In addition, the anode and the cathode of the electrolysis device of the present invention may each include a catalyst layer. In addition, in the cathode region, water vapor supplied with carbon dioxide generates a reduction product by an electroreduction reaction on the surface of the cathode. Thus, the cathode may include a gas diffusion layer to evenly supply humidified carbon dioxide gas to the cathode region. If the cathode includes a hydrophobic gas diffusion layer, it is possible to smoothly diffuse, distribute, and supply supplied carbon dioxide to the catalyst layer of the cathode. In addition, the hydrophobic gas diffusion layer effectively prevents moisture condensation, thereby allowing the supply of carbon dioxide to be continuously uniform, and at the same time, allowing an electrolysis reaction to smoothly progress. In addition, the catalyst layer may have a surface having a porous structure or the like to well exert gas permeation properties on the surface.

[0054] According to an embodiment of the present invention, the anode may include a catalyst active in the electrolysis of water, and the catalyst layer of the anode may include one or more selected from the group consisting of Pt, Au, Pd, Ir, Ag, Rh, Ru, Ni, Al, Mo, Cr, Cu, Ti, W, an alloy thereof, or a mixed metal oxide, e.g., Ta_20_5, $Ir0_2$, etc., for an oxygen generation reaction. Specifically, in the carbon dioxide electrolysis device of the present invention, the anode may include titanium (Ti)

coated with iridium oxide (IrO_2).

[0055] In addition, since a carbon dioxide reduction reaction which occurs in the cathode competes with a hydrogen generation reaction, a voltage required for the hydrogen generation reaction is high and a catalyst active in the carbon dioxide reduction reaction may be included. The catalyst layer of the cathode may include one or more selected from the group consisting of Sn, an Sn alloy, Al, Au, Ag, C, Cd, Co, Cr, Cu, an Cu alloy, Ga, Hg, In, Mo, Nb, Ni, $NiCo_2O_4$, an Ni alloy, an Ni-Fe alloy, Pb, Rh, Ti, V, W, Zn, and a mixture thereof. Specifically, in the carbon dioxide electrolysis device of the present invention, the cathode may contain silver (Ag).

[0056] In addition, as the separator, a cation exchange membrane (CEM) or an anion exchange membrane (AEM) may be included. Specifically, the cation exchange membrane may serve as a membrane which prevents a reduction material generated in the cathode by catalysis from being transferred to the anode and oxidized, and may be a separation phase which suppresses transmission of an anion and allows the transmission of a cation such as a hydrogen ion (H^+). In addition, a hydrogen ion (H^+) is generated in the anode by oxidizing water, and an excessive amount of the hydrogen ion flows to the cathode to saturate an active portion of the catalyst in which carbon dioxide is converted, which may cause a problem in which the conversion rate of carbon dioxide is decreased. At this time, the anion exchange membrane may reduce the amount of the hydrogen ion flowing to the cathode. The anion exchange membrane blocks the transfer of the hydrogen ion, and thus, may prevent carbon dioxide conversion performance of the cathode from degrading, and may refer to a separation phase which allows the transmission of an anion such as OH^-, HCO_3^-, and CO_3^{2-}.

[0057] In addition, as the electrolyte, one or more electrolyte selected from the group consisting of $KHCO_3$, K_2CO_3, KOH, KCl, $KClO_4$, K_2SiO_3, Na_2SO_4, $NaNO_3$, NaCl, NaF, $NaClO_4$ $CaCl_2$, Cs_2CO_3, H_3PO_4, $KHPO_4$, guanidinium cation, H^+ cation, alkali metal cation, ammonium cation, alkyl ammonium cation, halide ion, alkyl amine, borate, carbonate, guanidinium derivative, nitrite, nitrate, phosphate, polyphosphate, perchlorate, silicate, sulfate, tetraalkyl ammonium salt, or an aqueous solution containing a mixture thereof may be used, and specifically, the electrolyte of the carbon dioxide electrolysis device of the present invention may include an aqueous solution containing one or more selected from the group consisting of KOH, $KHCO_3$, Cs_2CO_3, H_3PO_4, or a mixture of H_3PO_4 and $KHPO_4$.

[0058] In addition, the gas diffusion layer may use a porous body using a carbon material such as carbon fiber cloth, carbon fiber felt, carbon fiber paper, or the like, or a metal porous body made of a thin metal plate having a net structure such as expanded metal, metal mesh, or the like, and in the carbon dioxide electrolysis device of the present invention, the gas diffusion layer may use carbon fiber cloth.

[0059] According to an embodiment of the present invention, the electrolysis device may be utilized in all fields that require electrochemical conversion, and particularly, allows a desired product to be obtained by electrochemically decomposing carbon dioxide, and specifically, the electrolysis device may electrolyze carbon dioxide to produce one or more selected from the group consisting of carbon monoxide, ethylene, methane, formic acid, hydrocarbon, aldehyde, and alcohol.

[0060] Hereinafter, embodiments of the present invention will be described in detail so that those skilled in the art may easily carry out the present invention. However, the present invention may be embodied in many different forms, and is not limited to the embodiments set forth herein.

Example 1

[0061] A carbon dioxide electrolysis device having operating conditions described below was operated. A pressure of about 0.4 bar (=40 kPa) was applied to a cathode outlet to operate the carbon dioxide electrolysis device.

Reaction current density: 300 mA/cm^2 (constant current operation)
Reaction voltage: 1 V to 4 V
Reaction temperature: 40 °C
Reaction pressure: 1 atm (atmospheric pressure)
Anode catalyst: IrO_2 on Ti mesh
Cathode catalyst: Ag powder
Electrode area: 100 cm^2
Gas diffusion layer: Sigracet 39BB
Anode electrolyte: 0.5 M $KHCO_3$(200 ml/min)
Cathode reactant: 40 °C Humidified CO_2 gas
40 °C Humidified CO_2 gas supply flow 800 ml/min

Example 2

[0062] The same procedure as in Example 1 was performed, except that a pressure of about 0.20 bar (=20 kPa) was applied to the cathode outlet.

Example 3

[0063] The same procedure as in Example 1 was performed, except that a reaction current density of about 200 mA/cm^2 was applied.

Example 4

[0064] The same procedure as in Example 1 was performed, except that the reaction current density was about 200 mA/cm^2, the electrode area was about 1,000 cm^2, the 40 °C Humidified CO_2 gas supply flow was about 6,000 ml/min, and the flow rate of the anode electrolyte was about 2 L/min.

Example 5

[0065] The same procedure as in Example 1 was performed, except that the reaction current density was about 200 mA/cm^2, a pressure of about 0.50 bar (=50 kPa) was applied to the cathode outlet, the electrode area was about 1000 cm^2, the 40 °C Humidified CO_2 gas supply flow was about 18000 ml/min, and the flow rate of the anode electrolyte was about 3 L/min.

Example 6

[0066] The same procedure as in Example 1 was performed, except that a pressure of about 0.50 bar (=50 kPa) was applied to the cathode outlet, the electrode area was about 1000 cm^2, the 40 °C Humidified CO_2 gas supply flow was about 18000 ml/min, and the flow rate of the anode electrolyte was about 3 L/min.

Comparative Example 1

[0067] The same procedure as in Example 1 was performed, except that no pressure was applied to the cathode outlet.

Comparative Example 2

[0068] The same procedure as in Example 1 was performed, except that a pressure of about 0.60 bar (=60 kPa) was applied to the cathode outlet.

Comparative Example 3

[0069] The same procedure as in Example 1 was performed, except that no pressure was applied to the cathode outlet and a reaction current density of about 200 mA/cm^2 was applied.

Comparative Example 4

[0070] The same procedure as in Example 1 was performed, except that the reaction current density was about 200 mA/cm^2, the electrode area was about 1,000 cm^2, the 40 °C Humidified CO2 gas supply flow was about 6,000 ml/min, the flow rate of the anode electrolyte was about 2 L/min, and no pressure was applied to the cathode outlet.

Comparative Example 5

[0071] The same procedure as in Example 5 was performed, except that no pressure was applied to the cathode outlet.

<Experimental Examples>

[0072] A carbon dioxide electrolysis device was operated using the operation methods according to Examples 1 to 6 and Comparative Examples 1 to 4. Electrolysis was performed using the carbon dioxide electrolysis device, at which time the conversion rate (%) of carbon monoxide, the CO Faraday efficiency (%) of carbon monoxide, and the voltage were measured, and the measurement result values are shown in Table 1. In addition, a long-term performance evaluation was performed on Example 5 and Comparative Example 5, and the evaluation results are shown in FIGS. 1 to 3.

Measurement methods

(1) Conversion rate of carbon monoxide (%)

[0073] The conversion rate (%) was calculated as the ratio of produced carbon monoxide (CO) with respect to the amount of introduced carbon dioxide (CO_2) gas per hour.

(2) Faraday efficiency (%) of carbon monoxide

[0074] The gas composition at the cathode outlet was measured through Gas-Chromatography (GC) analysis. In addition, Faraday efficiency was calculated through the following equation.

[Equation 1]

$$FE_{product}(\%) = \frac{i_{product}}{i_{total}} \times 100 = \frac{V_{product} \times Q \times \frac{2Fp}{RT}}{i_{total}} \times 100$$

[0075] In Equation 1 above, Q is a flow rate at a cathode outlet, F is a Faraday constant, p is a pressure, T is a measurement temperature, and R is an ideal gas constant. A total current i_{total} is a value of the total current applied over time, and a current $i_{product}$ with respect to a product is a value calculated from a volume of gas $V_{product}$ measured through GC analysis.

(3) Voltage (V)

[0076] The application of a current and the measurement of a voltage were performed through a VSP potentiostat of BioLogic Co. An 80 A booster was mounted to apply a current corresponding to a large area. The application of the current was performed in stages of 200 mA/cm^2 and 300 mA/cm^2, respectively, and was maintained for a predetermined period of time, after which the voltage was recorded at the time when the time of 20 minutes had elapsed. At this time, the Gas-Chromatography (GC) analysis was simultaneously performed.

(4) Long-term performance evaluation

[0077] The carbon dioxide electrolysis devices of Example 5 and Comparative Example 5 were operated for at least 200 hours, and the conversion rate of carbon monoxide, the Faraday efficiency of carbon monoxide, the Faraday efficiency of hydrogen, the reaction current density and the overvoltage of Example 5, and the reaction current density and the overvoltage of Comparative Example 5 were measured in the same manner as in the above-described measurement methods.

[Table 1]

Classificat ion	Cathode inlet flow rate (ml/min)	Current density (mA/ cm^2)	Applied pressur e (bar)	Faraday efficie ncy (%)	Carbon dioxide convers ion rate	Overvol tage (V)
Example 1	800	300	0.4	89.0	25.35	-3.53
Example 2	800	300	0.2	91.3	26.01	-3.507
Example 3	800	200	0.4	93.6	17.78	-3.209
Example 4	6000	200	0.4	91.1	20.83	-4.613
Example 5	18000	200	0.3	92	19.8	-9.41
Example 6	18000	300	0.5	88	29.2	-10.1
Comparative Example 1	800	300	0	89.0	25.35	-3.778
Comparative Example 2	800	300	0.6	87.4	24.88	-3.561
Comparative Example 3	800	200	0	90.3	17.70	-3.286
Comparative Example 4	6000	200	0	89.7	20.52	-4.235

[0078] Referring to Table 1, in Examples 1 to 4, a suitable pressure was applied to the cathode outlet, in Comparative Examples 1, 3, and 4, no pressure was applied to the cathode outlet, and in Comparative Example 2, a pressure out of the suitable pressure range according to the method for operating an electrolysis device of the present invention was applied to the cathode outlet. When comparing Examples 1 to 2 with Comparative Examples 1 to 2, in all of which the same current density was applied, Examples 1 to 2 in which a suitable pressure was applied to the cathode outlet exhibited higher Faraday efficiency and carbon dioxide conversion rate, and lower overvoltage than Comparative Examples 1 and 2, so it can be confirmed that the electrolysis efficiency of Examples 1 and 2 is superior thereto. Comparative Example 1 exhibited the Faraday efficiency and the carbon dioxide conversion rate which are the same as those of Example 1, but had a higher overvoltage, so that it can be seen that the electrolysis efficiency of Comparative Example 1 was lower than that of Example 1. In addition, in Example 3 and Comparative Example 3, a current having a current density 200 mA/cm^2 was applied, and even in this case, it can be seen that the electrolysis efficiency of Example 3 in which a suitable pressure was applied to the cathode outlet was superior to that of Comparative Example 3 in which no pressure was applied. In addition, Example 4 and Comparative Example 4 has the same increase in electrode area and cathode inlet flow rate, and even in this case, it can be seen that the electrolysis efficiency of Example 4 in which a suitable pressure was applied to the cathode outlet was superior to that of Comparative Example 4 in which no pressure was applied.

[0079] In addition, referring to FIGS. 1 and 2, when the carbon dioxide electrolysis device of Example 5 was operated under the reaction current density condition of 200 mA/cm^2 for at least 200 hours, the Faraday efficiency of carbon monoxide was maintained constant at a value of about 88% to about 97%. In addition, the Faraday efficiency of hydrogen was maintained constant at a value of about 0% to about 4%. In addition, the overvoltage was maintained in the range between about -3.3 V to about -3.0 V for at least 200 hours. In FIG. 1, ● represents a voltage, and ♦ represents a current. In addition, in FIG. 2, ● represents Faraday efficiency of carbon dioxide, and ♦ represents Faraday efficiency of hydrogen.

[0080] In addition, a 200-hour interim on-off evaluation was conducted, and even in this case, it can be seen that the original high electrolysis efficiency level was restored. That is, if a predetermined back pressure is applied to a cathode outlet to maintain the pressure ratio between an anode inlet and the cathode outlet within the range of the present invention, it can be confirmed that the device may operate for a long period of time since the generation of a salt is suppressed.

[0081] On the other hand, referring to FIG. 3, in the case of the carbon dioxide electrolysis device of Comparative Example 5, it can be confirmed that the reaction current density rapidly decreased, and the overvoltage increased after 12 hours had elapsed, from which it can be confirmed that when a back pressure is not applied to a cathode outlet, the salt prevents a long-term operation. In FIG. 3, ● represents a voltage, and ♦ represents a current.

Claims

1. An electrolysis device comprising:

an electrolysis stack in which one or more electrolysis cells including an anode, a cathode, a separator, and an electrolyte solution are stacked;
an anode inlet connected to the anode to transfer the electrolyte solution; and
a cathode outlet connected to the cathode to discharge a product and an unreacted reactant from the cathode, wherein in the cathode outlet, a back pressure is applied to the product and the unreacted reactant discharged from the cathode outlet.

2. The electrolysis device of claim 1, wherein the back pressure is 10 kPa to 50 kPa.

3. The electrolysis device of claim 1, wherein the cathode outlet comprises a pressure control valve.

4. The electrolysis device of claim 1, wherein the electrolysis stack has an electrode area of 500 cm^2 to 5,000 cm^2.

5. The electrolysis device of claim 1, wherein the electrolyte solution has a loss flow rate of 0.1 L/day or less.

6. The electrolysis device of claim 1, wherein the electrolysis cell is a membrane electrode assembly having a zero-gap structure in which a gas diffusion layer, a cathode, a separator, and an anode with an electrolyte flow path are sequentially stacked.

7. The electrolysis device of claim 1, wherein the electrolysis device electrolyzes carbon dioxide.

8. The electrolysis device of claim 1, wherein the electrolysis device produces at least one selected from the group

consisting of carbon monoxide, ethylene, methane, formic acid, hydrocarbon, aldehyde, and alcohol.

9. A method for operating an electrolysis device, the method comprising:

supplying an electrolyte solution through an anode inlet to an electrolysis stack in which one or more electrolysis cells including an anode, a cathode, a separator, and an electrolyte solution are stacked, and supplying a reactant through a cathode inlet S1;
performing an electrolysis reaction on the reactant in the electrolysis stack S2; and
discharging a product produced by the electrolysis reaction of the step S2 and an unreacted reactant through a cathode outlet to the outside of the electrolysis stack S3,
wherein in the step S3, a back pressure of 10 kPa to 50 kPa is applied to the product and the unreacted reactant discharged through the cathode outlet.

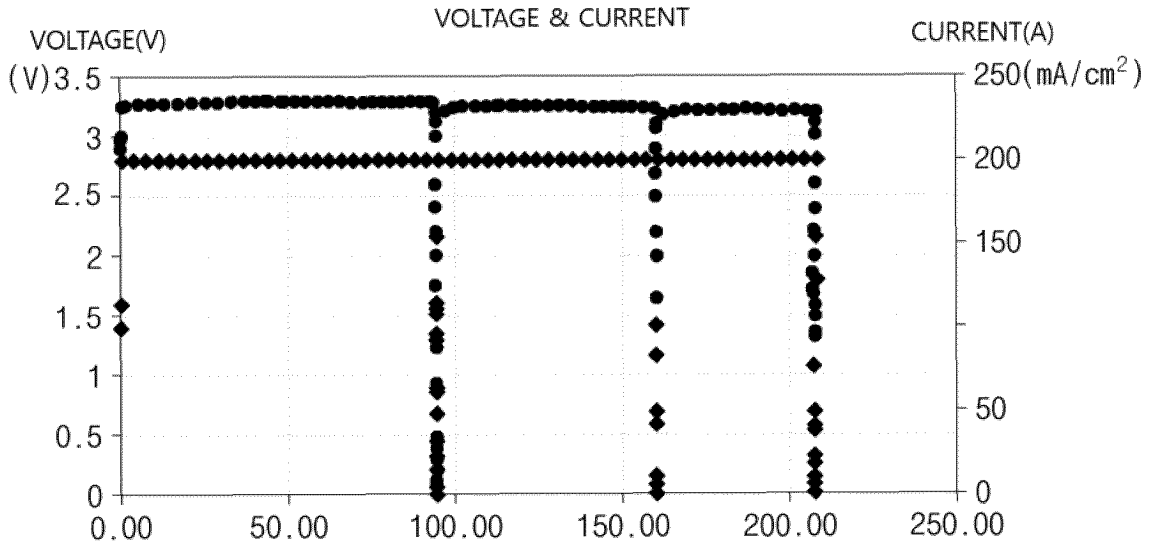
10. The method of claim 9, wherein the back pressure in the step S3 is 20 kPa to 40 kPa.

11. The method of claim 9, wherein in the step S1, the supply flow rate of the reactant is maintained constant while the electrolysis reaction is performed.

12. The method of claim 9, wherein the back pressure is controlled by opening and closing of a pressure control valve disposed in the cathode outlet.

13. The method of claim 9, wherein the unreacted reactant discharged in the step S3 are circulated back into the electrolysis stack.

[FIG. 1]


VOLTAGE & CURRENT
VOLTAGE(V)
CURRENT(A)
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2
1.5
1
0.5
0
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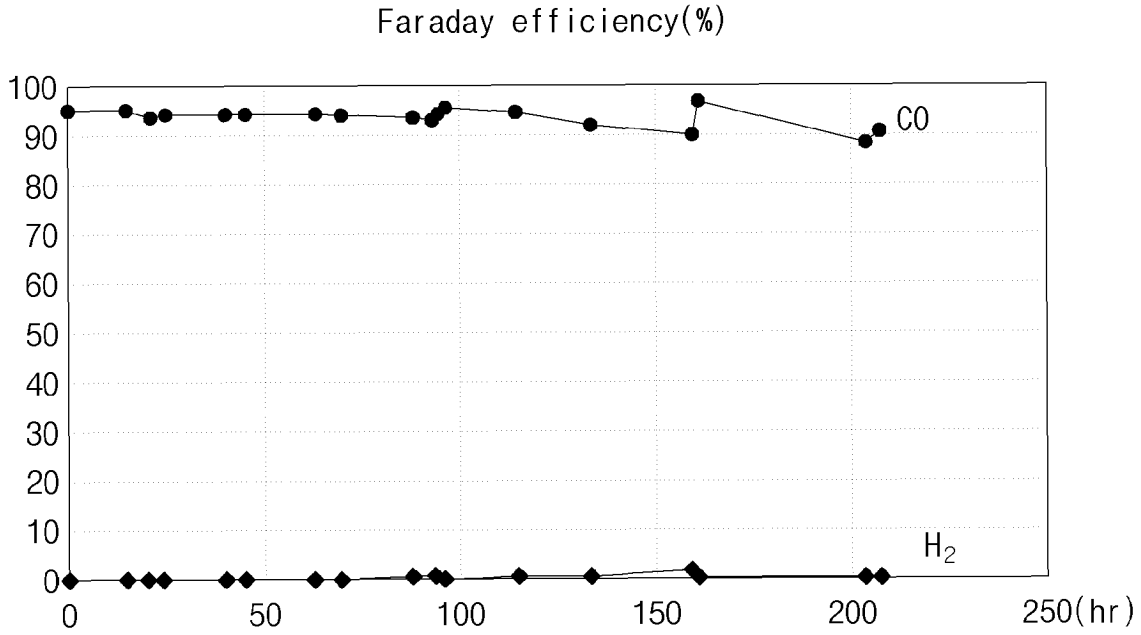
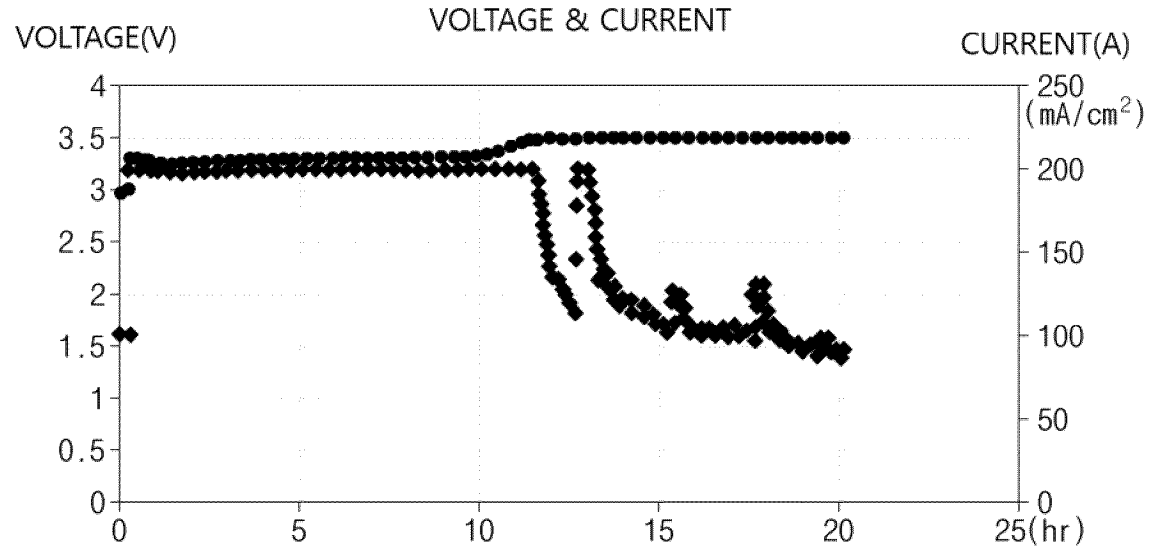
200
150
50
0
0.00
50.00
100.00
150.00
200.00
250.00

[FIG. 2]


Faraday efficiency(%)
100
90
80
70
60
50
40
30
20
10
0
CO
H2
0
50
100
150
200
250(hr)

[FIG. 3]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CURRENT(A)
(mA/cm²)
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3
2.5
2
1.5
1
0.5
0
250
200
150
100
50
0
0
5
10
15
20
25(hr)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2023/015125

A. CLASSIFICATION OF SUBJECT MATTER

C25B 15/08(2006.01)i; **C25B 15/02**(2006.01)i; **C25B 9/23**(2021.01)i; **C25B 11/032**(2021.01)i; **C25B 1/23**(2021.01)i; **C25B 3/26**(2021.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C25B 15/08(2006.01); C01B 32/50(2017.01); C25B 1/00(2006.01); C25B 1/04(2006.01); C25B 1/22(2006.01); C25B 15/02(2006.01); C25B 3/04(2006.01); C25B 9/08(2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

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

eKOMPASS (KIPO internal) & keywords: 전기분해(electrolysis), 배압(back pressure), 이산화탄소(carbon dioxide), 막전극 접합체(MEA), 전해액(electrolyte), 밸브(valve)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2020-045527 A (TOSHIBA CORP.) 26 March 2020 (2020-03-26) See claims 1 and 5; paragraphs [0008], [0011], [0014], [0030], [0034], [0037]-[0039], [0043] and [0087]; and figure 1.	1-13
A	JP 5787034 B2 (TOYOTA MOTOR CO., LTD.) 30 September 2015 (2015-09-30) See entire document.	1-13
A	KR 10-1793711 B1 (KOREA INSTITUTE OF ENERGY RESEARCH) 07 November 2017 (2017-11-07) See entire document.	1-13
A	KR 10-2014-0073007 A (KUMOH NATIONAL INSTITUTE OF TECHNOLOGY INDUSTRY-ACADEMIC COOPERATION FOUNDATION) 16 June 2014 (2014-06-16) See entire document.	1-13
A	JP 2018-510963 A (SIEMENS AKTIENGESELLSCHAFT) 19 April 2018 (2018-04-19) See entire document.	1-13

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
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"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 January 2024	**15 January 2024**
Name and mailing address of the ISA/KR **Korean Intellectual Property Office** **Government Complex-Daejeon Building 4, 189 Cheongsa-ro, Seo-gu, Daejeon 35208** Facsimile No. **+82-42-481-8578**	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2022)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2023/015125

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		WO 2016-124300 A1	11 August 2016

Form PCT/ISA/210 (patent family annex) (July 2022)

REFERENCES CITED IN THE DESCRIPTION

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