(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 4 570 961 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
18.06.2025 Bulletin 2025/25

(21) Application number: **24823756.2**

(22) Date of filing: **14.06.2024**

(51) International Patent Classification (IPC):
C25B 9/19 *(2021.01)* ***C25B 3/26*** *(2021.01)*
C25B 15/08 *(2006.01)* ***C25B 9/60*** *(2021.01)*
C25B 3/03 *(2021.01)* ***C25B 3/07*** *(2021.01)*

(52) Cooperative Patent Classification (CPC):
C25B 3/03; C25B 3/07; C25B 3/26; C25B 9/19; C25B 9/60; C25B 15/08

(86) International application number:
PCT/KR2024/008258

(87) International publication number:
WO 2024/258240 (19.12.2024 Gazette 2024/51)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
GE KH MA MD TN

(30) Priority: **16.06.2023 KR 20230077536**

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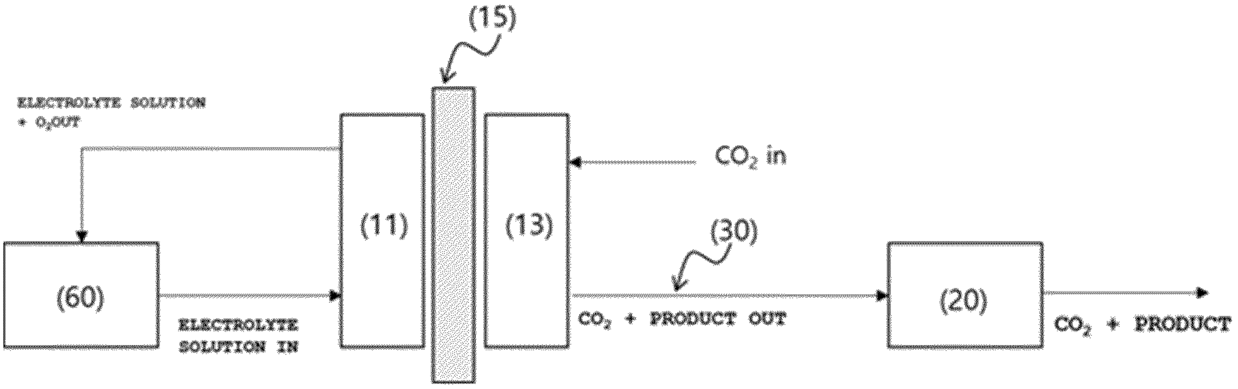
(54) ELECTROLYSIS DEVICE

(57) The present invention relates to an electrolysis device including an electrolysis cell having a gas diffusion layer, a cathode, a separation membrane, an anode, and an electrolyte solution, and outside the electrolysis cell, an acid solution reservoir connected by a discharge flow path for discharging a product from the cathode, wherein the separation membrane is a cation separation membrane.

[FIG. 1]



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Description

TECHNICAL FIELD

Cross-reference to Related Applications

[0001] This application claims the benefit of Korean Patent Application No. 10-2023-0077536, filed on June 16, 2023, 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 electrochemically reducing carbon dioxide.

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, and is thus 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 separation membrane. 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] Meanwhile, in a typical electrolysis device, OH^- is produced by a side reaction in a cathode during a carbon dioxide electrolysis process, and the OH^- is reacted again with supplied carbon dioxide and produces a carbonate (HCO_3^-). Therefore, the typical electrolysis device has a problem in that supplied carbon dioxide produces a carbonate without being converted into a desired product, which results in causing the loss of the carbon dioxide. In addition, the typical electrolysis device has a problem in that the efficiency of the electrolysis is reduced since the carbonate is diffused into an anode by passing through an anion exchange membrane and carbon dioxide is produced through an oxidation reaction in the anode.

(Patent Document 001) KR 10-2018-0133688 A

DISCLOSURE OF THE INVENTION

TECHNICAL PROBLEM

[0006] An object to be achieved by the present invention is to provide an electrolysis device in which carbon dioxide is separated again from a carbonate produced by a side reaction during electrolysis of carbon dioxide, thereby preventing the loss of carbon dioxide converted into a carbonate and improving the yield of a product.

TECHNICAL SOLUTION

[0007] The present invention provides an electrolysis device.

(1) The present invention provides an electrolysis device including an electrolysis cell having a gas diffusion layer, a

cathode, a separation membrane, an anode, and an electrolyte solution, and outside the electrolysis cell, an acid solution reservoir connected by a discharge flow path for discharging a product from the cathode, wherein the separation membrane is a cation separation membrane.

(2) In (1) above, the present invention provides an electrolysis device, wherein the acid solution reservoir includes an acidic solution containing one or more selected from the group consisting of phosphoric acid, hydrochloric acid, sulfuric acid, nitric acid, acetic acid, citric acid, and oxalic acid.

(3) In (1) or (2) above, the present invention provides an electrolysis device, wherein the electrolyte solution is an aqueous solution containing one or more selected from the group consisting of Cs_2CO_3, $CsHCO_3$, Cs_2SO_4, CsCl, $CsNO_3$, K_2CO_3, $KHCO_3$, K_2SO_4, K_3PO_4, KCl, KNO_3, Na_2CO_3, $NaHCO_3$, Na_2SO_4, Na_3PO_4, NaCl, and $NaNO_3$.

(4) In any one of (1) to (3) above, the present invention provides an electrolysis device, wherein the electrolysis cell is a zero-gap membrane electrode assembly cell in which the gas diffusion layer, the cathode, the separation membrane, and an anode with an anode liquid flow path formed therein are sequentially stacked.

(5) In any one of (1) to (4) above, the present invention provides an electrolysis device, wherein a product produced by an electrolysis reaction in the cathode is transferred to the acid solution reservoir through the discharge flow path, wherein the product includes carbon monoxide, water vapor, and a salt.

(6) In (5) above, the present invention provides an electrolysis device, wherein carbon dioxide produced from the salt in the acid solution reservoir is supplied to the electrolysis cell.

(7) In (5) or (6) above, the present invention provides an electrolysis device, wherein the salt is a carbonate.

(8) In any one of (1) to (7) above, the present invention provides an electrolysis device, wherein the electrolysis device electrolyzes carbon dioxide.

(9) In (8) above, the present invention provides an electrolysis device, wherein the carbon dioxide is supplied in a state including water vapor when supplied to the electrolysis cell.

(10) In any one of (1) to (9) above, the present invention provides an electrolysis device, wherein the electrolysis device electrolyzes carbon dioxide, thereby producing one or more selected from the group consisting of carbon monoxide, ethylene, methane, formic acid, hydrocarbon, aldehyde, and alcohol.

ADVANTAGEOUS EFFECTS

[0008] An electrolysis device of the present invention connects an acid solution reservoir with an electrolysis cell, thereby separating carbon dioxide from a salt produced by a side reaction in the acid solution reservoir, and thus, may prevent the loss of carbon dioxide.

[0009] In addition, the electrolysis device of the present invention reduces the loss of carbon dioxide, and thus, may improve the electrolysis efficiency of carbon dioxide, thereby increasing the yield of a product.

BRIEF DESCRIPTION OF THE DRAWING

[0010] FIG. 1 is a schematic diagram of a carbon dioxide electrolysis device according to the present invention.

MDOE FOR CARRYING OUT THE INVENTION

[0011] 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.

[0012] The terms used herein are only used to describe exemplary embodiments, and are not intended to limit the present invention. Singular expressions include plural expressions unless the context clearly indicates otherwise.

[0013] It will be further understood that the terms "include," "comprise," or "have" when used in the present specification, 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.

[0014] The present invention provides an electrolysis device including an electrolysis cell having a gas diffusion layer, a cathode 13, a separation membrane 15, an anode 11, and an electrolyte solution, and outside the electrolysis cell, an acid solution reservoir 20 connected by a discharge flow path 30 for discharging a product from the cathode 13, wherein the separation membrane 15 is a cation separation membrane.

[0015] According to an embodiment of the present invention, the electrolysis device may be used in all fields of electrochemical conversion, and the electrolysis device may be a fuel cell, a device capable of producing useful chemical materials 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.

[0016] As described in the background art, an electrolysis cell having a typical structure in which an electrolyte solution flows in the front part of a cathode has a problem in that OH^- produced by a side reaction during a reduction process of carbon dioxide reacts again with the carbon dioxide to produce a carbonate (HCO_3^-), and thus, the carbon dioxide is lost, wherein the problem is solvable by allowing an acidic electrolyte solution to flow in the front part of the cathode, but in this case, additional resistance occurs by the acidic electrolyte solution, which creates an additional problem in which a voltage increases. In addition, as a separation membrane to be included in a carbon dioxide electrolysis cell, an anion exchange membrane has been mainly used, and the anion exchange membrane is fast in ion transfer, and thus, has excellent carbon dioxide conversion efficiency, but has very low mechanical strength, and in addition, the carbonate passes through the anion exchange membrane and is diffused to an anode and carbon dioxide is produced through an oxidation reaction in the anode, so that there is a problem in that the efficiency of the electrolysis is degraded.

[0017] Therefore, the inventor of the present invention developed an electrolysis device of the present invention in which a produced carbonate is not diffused into the anode 11, and carbon dioxide is separated again from the produced carbonate, thereby reducing the loss of supplied carbon dioxide. Specifically, the electrolysis device includes the electrolysis cell and the acid solution reservoir 20 connected to the outside of the electrolysis cell. The electrolysis device includes the cathode 13 and the anode 11, wherein the gas diffusion layer may be disposed in close proximity to the cathode 13, and may include the separation membrane 15 disposed between the cathode 13 and the anode 11 and the electrolyte solution together. In addition, the electrolysis device according to the present invention may include an electrolysis cell having a structure of a zero-gap membrane electrode assembly to be described later. The electrolysis cell having a structure of a zero-gap membrane electrode assembly has a structure in which an electrolyte solution does not flow in the front part of the cathode 13, but the electrolyte solution flows only in the front part of the anode 11, so that the additional problem in which a voltage increases during an electrolysis reaction may be solved. In addition, the electrolysis cell may include a cation exchange membrane to prevent the produced carbonate from being transported toward the anode 11.

[0018] FIG. 1 is a schematic diagram of a carbon dioxide electrolysis device according to the present invention.

[0019] According to an embodiment of the present invention, the cathode 13 is connected to a supply line to which a reactant is supplied, and the discharge flow path 30 through which a product produced after electrolysis is discharged. The reactant may be carbon dioxide, and the carbon dioxide may be in a gaseous state, and may include water vapor of about 40 °C to 60 °C. In addition, the product is produced by electrolyzing the carbon dioxide, and may be one or more selected from the group consisting of carbon monoxide, ethylene, methane, formic acid, hydrocarbon, aldehyde, and alcohol. Unreacted carbon dioxide, the water vapor, and the carbonate produced by a side reaction may be further discharged together with the product discharged from the discharge flow path 30.

[0020] Referring to FIG. 1, the acid solution reservoir 20 is connected to the discharge flow path 30, and carbon dioxide may be separated again from the carbonate by an acidic solution filled in the acid solution reservoir 20. Specifically, hydrogen ions (H^+) of the acidic solution contained in the acid solution reservoir 20 and a carbonate (HCO_3^-) may react to each other to produce water and carbon dioxide. In addition, the acid solution reservoir 20 may include an acidic solution containing one or more selected from the group consisting of phosphoric acid, hydrochloric acid, sulfuric acid, nitric acid, acetic acid, citric acid, and oxalic acid. The acidic solution may serve to reproduce carbon dioxide by reacting with a produced carbonate, and compared to a typical electrolysis device, the electrolysis device of the present invention further includes the acid solution reservoir 20 to reproduce carbon dioxide from a carbonate, and thus, may improve electrolysis efficiency and reduce the amount of carbon dioxide lost to the carbonate.

[0021] According to an embodiment of the present invention, the separation membrane 15 is a cation separation membrane 15, and specifically, may be a Nafion separation membrane 15. The cation separation membrane 15 may serve to prevent a carbonate produced from the cathode 13 from diffusing toward the anode 11. Furthermore, if the separation membrane 15 is an anion separation membrane 15, a carbonate is diffused toward the anode 11, so that the transport of the carbonate to the acid solution reservoir 20 is not facilitated, which may degrade overall electrolysis efficiency, and may increase carbon dioxide loss.

[0022] According to an embodiment of the present invention, the electrolyte solution may be an acidic or neutral electrolyte solution, and may be an aqueous solution containing cations (Na^+, K^+, or Cs^+). Illustratively, it may be Cs_2CO_3, $CsHCO_3$, Cs_2SO_4, CsCl, $CsNO_3$, K_2CO_3, $KHCO_3$, K_2SO_4, K_3PO_4, KCl, KNO_3, Na_2CO_3, $NaHCO_3$, Na_2SO_4, Na_3PO_4, NaCl, or $NaNO_3$.

[0023] According to an embodiment of the present invention, the electrolysis cell may be a zero-gap membrane electrode assembly cell in which the gas diffusion layer, the cathode 13, the separation membrane 15, and the anode 11 having a liquid flow path of the anode 11 are sequentially stacked. Specifically, in order to increase a driving voltage and current efficiency, the zero-gap membrane electrode assembly may be formed in a very thin valve shape in which the gas diffusion layer, the cathode 13, the separation membrane 15, and the anode 11 having a liquid flow path of the anode 11 are sequentially stacked.

[0024] A typical electrolysis cell has a shape of a gap structure since an electrode and a separation membrane are spaced apart from each other by several mm intervals, but the above-described zero gap is an electrolysis cell of a sandwich shape without an interval between an electrode and a separation membrane since a cathode electrode and an anode electrode are in contact with each other with a separation membrane interposed therebetween, so that the electrolytic cell of a zero-gap shape may decrease solution ion resistance due to the presence of an electrolyte, and may reduce an increase in mass transfer resistance due to a produced gas when implementing a large-area electrode.

[0025] In addition, an electrolyte solution flowing toward the cathode 13 is called a cathode 13 liquid, and an electrolyte solution flowing toward the anode 11 is called an anode 11 liquid, and the zero-gap membrane electrode assembly may not include the cathode 13 liquid, but may include only the anode 11 liquid. The zero-gap membrane electrode assembly minimizes the gap between the cathode 13, the anode 11, and the separation membrane 15, and thus, may have the advantage of being able to accelerate the transport of ions, decrease overvoltage, and increase current efficiency. In addition, in this case, separation plates may be disposed on both sides of the zero-gap membrane electrode assembly to form one cell.

[0026] According to an embodiment of the present invention, the discharge flow path 30 transports a product produced in the cathode 13 by an electrolysis reaction to the acid solution reservoir 20, and the product may include carbon dioxide, carbon monoxide, water vapor, and a salt. In addition, the carbon dioxide produced in the acid solution reservoir 20 may be supplied to the electrolysis cell.

[0027] The carbon dioxide produced by separating carbon dioxide from a carbonate in the acid solution reservoir 20 may be supplied back to the cathode 13 through a supply line. The electrolysis device of the present invention separates carbon dioxide from a carbonate by means of the acid solution reservoir 20, and circulates the carbon dioxide into the electrolysis cell to reduce the loss of carbon dioxide, and to increase electrolysis efficiency.

[0028] Hereinafter, the decomposition principle of the electrolysis device and each component of the electrolysis device will be described.

[0029] 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 produce oxygen, at which time, a hydrogen ion is produced. The hydrogen ion produced in the anode is transferred to the cathode through the electrolyte solution, 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 produce a product. In addition, the separation membrane may be disposed between the anode and the cathode. The separation membrane 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.

[0030] 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.

[0031] 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 electrolysis device of the present invention, the anode may include titanium (Ti) coated with an iridium oxide (IrO_2).

[0032] 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, a 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 electrolysis device of the present invention, the cathode may contain silver (Ag).

[0033] In addition, the separation membrane, as described above, may include a cation exchange membrane CEM, and specifically, may be a Nafion exchange membrane. 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^+).

[0034] In addition, the electrolyte solution, as described above, may be an electrolyte solution according to the present invention, and specifically, may be an acidic electrolyte solution, and more specifically, may be an aqueous solution containing cesium hydrocarbonate. The electrolyte solution composition may include the electrolyte solution in 0.1 M to 15.0 M, preferably 0.25 M to 10.0 M. The concentration of the electrolyte solution is related to the production efficiency of a product (production efficiency of a target product relative to an applied current density) and a voltage. The higher the concentration of the electrolyte solution, the lower the generated voltage, required voltage, or overvoltage, but the above-described conditions are preferable in order to minimize an increase in manufacturing cost and production of additional products due to a side reaction.

[0035] 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 electrolysis device of the present invention, the gas diffusion layer may use carbon fiber cloth.

[0036] 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.

[0037] 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

[0038] A carbon dioxide electrolysis device having operating conditions described below was operated. A carbon dioxide electrolysis device was operated, which is a membrane electrode assembly having a zero-gap structure in which an anode, a cation separation membrane (type: Nafion®212), a cathode, and a gas diffusion layer are sequentially stacked, and which includes an acid solution reservoir connected to the outside of the cathode and the membrane electrode assembly and filled with an acidic solution (85%, H_3PO_4).

Reaction current density: 100 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 solution: 1.0 M $CsHCO_3$ (25 ml/min)
Cathode reactant: 40 °C Humidified CO_2 gas (200 ccm)
40 °C Humidified CO_2 gas supply flow 200 ml/min

Example 2

[0039] A carbon dioxide electrolysis device was operated under the same conditions as in Example 1, except that the reaction current density was 200 mA/cm^2.

Example 3

[0040] A carbon dioxide electrolysis device was operated under the same conditions as in Example 1, except that the reaction current density was 300 mA/cm^2.

Comparative Example 1

[0041] A carbon dioxide electrolysis device was operated under the same conditions as in Example 1, except that an anion exchange membrane was used instead of the cation exchange membrane and an acid solution reservoir was not included.

Comparative Example 2

[0042] A carbon dioxide electrolysis device was operated under the same conditions as in Example 2, except that an anion exchange membrane was used instead of the cation exchange membrane and an acid solution reservoir was not included.

Comparative Example 3

[0043] A carbon dioxide electrolysis device was operated under the same conditions as in Example 3, except that an anion exchange membrane was used instead of the cation exchange membrane and an acid solution reservoir was not included.

Comparative Example 4

[0044] A carbon dioxide electrolysis device was operated under the same conditions as in Example 1, except that an acid solution reservoir was not included.

Comparative Example 5

[0045] A carbon dioxide electrolysis device was operated under the same conditions as in Example 2, except that an acid solution reservoir was not included.

Comparative Example 6

[0046] A carbon dioxide electrolysis device was operated under the same conditions as in Example 3, except that an acid solution reservoir was not included.

Experimental Examples

[0047] A product resulting from a carbon dioxide reduction reaction performed through the carbon dioxide electrolysis device according to each of Examples 1 to 3 and Comparative Examples 1 to 6 was analyzed by gas chromatography. At this time, the amount of carbon dioxide initially introduced was compared with the amount of produced carbon dioxide, and the amount of carbon dioxide lost without being electrochemically reduced was measured. In addition, Faraday efficiency was measured for carbon monoxide and hydrogen according to the following measurement methods, and the measured properties are each described in Table 1 below.

(1) Carbon dioxide loss rate (CO_2 loss, %)

[0048] The gas composition at the discharge flow path was measured through Gas-Chromatography (GC) analysis. The flow rate (mL/min) of a discharged gas was multiplied by the percentage (%) of carbon dioxide measured through GC analysis, thereby measuring a flow rate Q_{CO2}.f of discharged CO_2 after electrochemical conversion, which was compared with an initial input flow rate Q_{CO2}.i to measure the total amount of CO_2 used (CO_2 used, %). Since the conversion ratio of CO during the CO_2 reduction reaction was 1:1, assuming that a flow rate Qco of a carbon monoxide gas measured by GC analysis is equal to the amount (CO_2 conv, %) of electrochemically converted CO_2, the remainder obtained by subtracting the conversion amount from the amount of CO_2 used was calculated as CO_2 loss. The measured value was calculated through the following Equation 1.

[Equation 1]

$$CO_2\ Used\ (\%) = \left(1 - \frac{Q_{CO2,f}}{Q_{CO2,i}}\right) \times 100$$

$$CO_2\ Conv\ (\%) = \frac{Q_{CO}}{Q_{CO2,i}} \times 100$$

$$CO_2\ Loss\ (\%) = CO_2\ Used\ (\%) - CO_2\ Conv\ (\%)$$

(2) Carbon monoxide Faraday efficiency (%)

[0049] The gas composition at the discharge flow path was measured through Gas-Chromatography (GC) analysis. In addition, Faraday efficiency was calculated through the following equation.

[Equation 2]

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

[0050] In Equation 2 above, Q is a flow rate at a discharge flow path, 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) Hydrogen Faraday efficiency (%)

[0051] The hydrogen Faraday efficiency was measured and calculated in the same way as the above-described carbon monoxide Faraday efficiency (2).

[Table 1]

Classification	Current density (mA/cm^2)	Exchange membrane type/ whether acid solution reservoir is included (O/X)	Hydrogen Faraday efficiency (%)	Carbon monoxide Faraday efficiency (%)	Carbon dioxide loss rate (%)
Example 1	100	Cation exchange membrane/O	0.80	100.15	4.72
Example 2	200	Cation exchange membrane/O	0.90	91.75	4.09
Example 3	300	Cation exchange membrane/O	3.31	84.10	4.41
Comparative Example 1	100	Anion exchange membrane/X	0.56	100.19	11.04
Comparative Example 2	200	Anion exchange membrane/X	0.67	95.39	20.46
Comparative Example 3	300	Anion exchange membrane/X	0.86	92.04	29.57
Comparative Example 4	100	Cation exchange membrane/X	2.85	100.19	14.01
Comparative Example 5	200	Cation exchange membrane/X	2.22	92.01	29.00
Comparative Example 6	300	Cation exchange membrane/X	6.31	81.33	41.37

[0052] Referring to Table 1, in the case of Examples 1 to 3 which include an acid solution reservoir, compared to Comparative Examples 1 to 6 which do not include an acid solution reservoir, the carbon monoxide Faraday efficiency remained at the same level, and at the same time, the carbon dioxide loss rate was significantly low.

[0053] That is, the electrolysis device of the present invention separates carbon dioxide again from a carbonate by including an acid solution reservoir, and thus, may significantly reduce the loss of the carbon dioxide converted into the carbonate and have high electrolysis efficiency. In contrast, in the case of Comparative Examples 1 to 3 which use an anion exchange membrane or Comparative Examples 4 to 6 which use a cation exchange membrane but do not include an acid solution reservoir, it can be seen that the amount of carbon dioxide lost by being converted into a carbonate is large, so that the electrolysis efficiency is degraded.

11: Anode
13: Cathode
15: Separation membrane
20: Acid solution reservoir
30: Discharge flow path
60: Gas-liquid separator

Claims

1. An electrolysis device comprising:

an electrolysis cell including a gas diffusion layer, a cathode, a separation membrane, an anode, and an electrolyte solution; and
outside the electrolysis cell, an acid solution reservoir connected by a discharge flow path for discharging a product from the cathode,
wherein the separation membrane is a cation separation membrane.

2. The electrolysis device of claim 1, wherein the acid solution reservoir comprises an acidic solution containing one or more selected from the group consisting of phosphoric acid, hydrochloric acid, sulfuric acid, nitric acid, acetic acid, citric acid, and oxalic acid.

3. The electrolysis device of claim 1, wherein the electrolyte solution is an aqueous solution containing one or more selected from the group consisting of Cs_2CO_3, $CsHCO_3$, Cs_2SO_4, CsCl, $CsNO_3$, K_2CO_3, $KHCO_3$, K_2SO_4, K_3PO_4, KCl, KNO_3, Na_2CO_3, $NaHCO_3$, Na_2SO_4, Na_3PO_4, NaCl, and $NaNO_3$.

4. The electrolysis device of claim 1, wherein the electrolysis cell is a zero-gap membrane electrode assembly cell in which the gas diffusion layer, the cathode, the separation membrane, and an anode with an anode liquid flow path formed therein are sequentially stacked.

5. The electrolysis device of claim 1, wherein a product produced by an electrolysis reaction in the cathode is transported to the acid solution reservoir through the discharge flow path, wherein the product includes carbon monoxide, water vapor, and a salt.

6. The electrolysis device of claim 5, wherein carbon dioxide produced from the salt in the acid solution reservoir is supplied to the electrolysis cell.

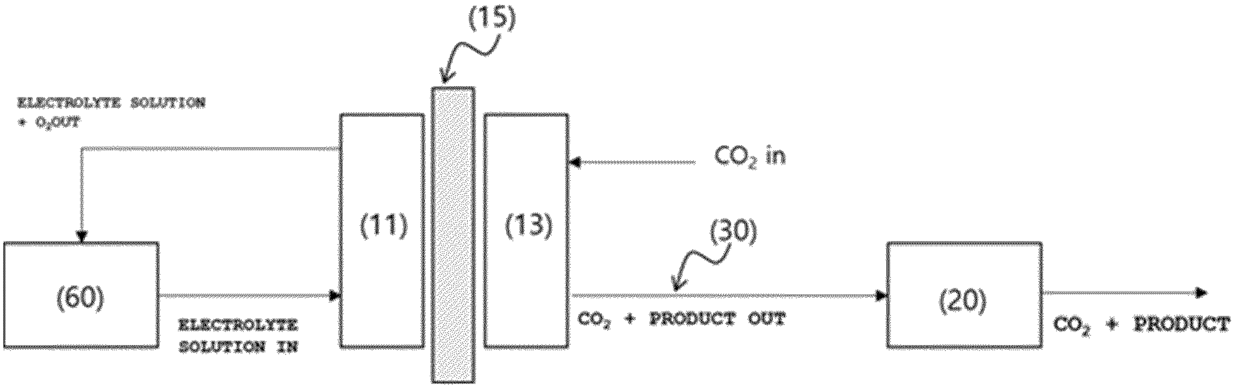
7. The electrolysis device of claim 5, wherein the salt is a carbonate.

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

9. The electrolysis device of claim 8, wherein the carbon dioxide is supplied in a state including water vapor when supplied to the electrolysis cell.

10. The electrolysis device of claim 1, wherein the electrolysis device electrolyzes carbon dioxide, thereby producing one or more selected from the group consisting of carbon monoxide, ethylene, methane, formic acid, hydrocarbon, aldehyde, and alcohol.

[FIG. 1]


(15)
ELECTROLYTE SOLUTION
+ O2OUT
CO2 in
(11)
(13)
(30)
(60)
ELECTROLYTE
SOLUTION IN
CO2 + PRODUCT OUT
(20)
CO2 + PRODUCT

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2024/008258

A. CLASSIFICATION OF SUBJECT MATTER

C25B 9/19(2021.01)i; **C25B 3/26**(2021.01)i; **C25B 15/08**(2006.01)i; **C25B 9/60**(2021.01)i; **C25B 3/03**(2021.01)i; **C25B 3/07**(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 9/19(2021.01); B01D 61/44(2006.01); C25B 1/00(2006.01); C25B 1/01(2021.01); C25B 1/26(2006.01); C25B 15/02(2006.01); C25B 3/04(2006.01); C25B 3/25(2021.01); C25B 9/00(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), 산성용액(acidic solution), 이산화탄소(carbon dioxide, CO2), 양이온 분리막(cation exchange membrane, CEM), 제로갭(zero gap)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	KR 10-2022-0079553 A (COVESTRO INTELLECTUAL PROPERTY GMBH & CO. KG) 13 June 2022 (2022-06-13) See abstract; paragraphs [0001], [0012], [0080], [0087], [0092], [0101]-[0106], [0109], [0116] and [0131]; claims 1 and 22; and figures 1-2.	1-4,8,10 5-7,9
Y	KR 10-2021-0086528 A (KOREA INSTITUTE OF ENERGY RESEARCH) 08 July 2021 (2021-07-08) See abstract; paragraph [0003]; and claims 1 and 5.	5-7,9
X	JP 2019-167556 A (TOSHIBA CORP.) 03 October 2019 (2019-10-03) See abstract; paragraphs [0003], [0018], [0024], [0028], [0029], [0036], [0037], [0047], [0051] and [0063]; and figure 7.	1-3,5-8,10
A	JP 2020-045527 A (TOSHIBA CORP.) 26 March 2020 (2020-03-26) See paragraphs [0003], [0030] and [0034]; and figure 3.	1-10

☑ 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
“E” earlier application or patent but published on or after the international filing date
“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
“O” document referring to an oral disclosure, use, exhibition or other means
“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 **19 September 2024**	Date of mailing of the international search report **19 September 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.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2024/008258

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 10-2017-0117933 A (TECHWIN CO., LTD.) 24 October 2017 (2017-10-24) See abstract; claims 1-10; and figures 3a-5b.	1-10

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2024/008258

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
KR 10-2022-0079553 A	13 June 2022	CN 114450436 A	06 May 2022
		EP 3805429 A1	14 April 2021
		EP 4041939 A1	17 August 2022
		JP 2022-551135 A	07 December 2022
		US 2024-0084462 A1	14 March 2024
		WO 2021-069470 A1	15 April 2021
KR 10-2021-0086528 A	08 July 2021	KR 10-2508484 B1	08 March 2023
JP 2019-167556 A	03 October 2019	JP 6818711 B2	20 January 2021
		US 11286573 B2	29 March 2022
		US 2020-0002821 A1	02 January 2020
		WO 2019-181002 A1	26 September 2019
JP 2020-045527 A	26 March 2020	EP 3626859 A1	25 March 2020
		EP 3626859 B1	10 August 2022
		JP 6951310 B2	20 October 2021
		US 11946150 B2	02 April 2024
		US 2020-0087803 A1	19 March 2020
		US 2022-0380916 A1	01 December 2022
KR 10-2017-0117933 A	24 October 2017	KR 10-1825087 B1	02 February 2018

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Patent documents cited in the description

- KR 1020230077536 **[0001]**