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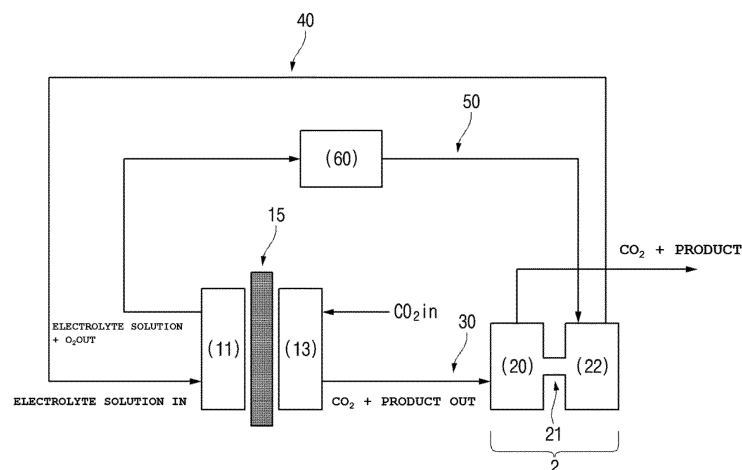
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(54) **ELECTROLYSIS DEVICE**

(57) The present invention relates to an electrolysis device including an electrolysis cell including a gas diffusion layer, a cathode, a cation separation membrane, an anode, and an electrolyte solution, and outside of the electrolysis cell, a reservoir connected by a discharge

flow path for discharging a product from the cathode, wherein an acidic solution included in the reservoir and an electrolyte solution included in the electrolysis cell are homogeneous solutions.

[FIG. 1]



Description**TECHNICAL FIELD****Cross-reference to Related Applications**

[0001] This application claims the benefit of Korean Patent Application No. 10-2023-0077537, 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.

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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, and which may be driven for a long period of time by adjusting the overall ion balance of the electrolysis device.

TECHNICAL SOLUTION

[0007] The present invention provides an electrolysis device.

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

cathode, a cation separation membrane, an anode, and an electrolyte solution, and outside the electrolysis cell, a reservoir connected by a discharge flow path for discharging a product from the cathode, wherein an acidic solution contained in the reservoir and the electrolyte solution contained in the electrolysis cell are homogeneous solutions.

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

(3) In (2) above, the present invention provides an electrolysis device, wherein the salt includes 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 reservoir comprises an acid solution storage and an electrolyte solution storage connected to the acid solution storage, wherein the electrolyte solution storage is connected to the anode by a solution exchange flow path.

(5) In (4) above, the present invention provides an electrolysis device, wherein the solution exchange flow path includes a solution exchange first flow path for transferring an acidic solution from the electrolyte solution storage to the anode, and a solution exchange second flow path for transferring an electrolyte solution from the anode to the electrolyte solution storage.

(6) In any one of (1) to (5) 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.

(7) In any one of (1) to (6) above, the present invention provides an electrolysis device, wherein a product produced by an electrolysis reaction in the cathode is transferred to the reservoir through the discharge flow path, wherein the product includes carbon monoxide, water vapor, and a salt.

(8) In (7) above, the present invention provides an electrolysis device, wherein carbon dioxide produced from the salt in the reservoir is supplied to the electrolysis cell.

(9) In (7) or (8) above, the present invention provides an electrolysis device, wherein the salt is a carbonate.

(10) In any one of (1) to (9) above, the present invention provides an electrolysis device, wherein the electrolysis device electrolyzes carbon dioxide.

(11) In (10) 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.

(12) In any one of (1) to (11) 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 a reservoir containing an acidic solution with an electrolysis cell, thereby separating carbon dioxide from a salt produced by a side reaction, 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.

[0010] In addition, the electrolysis device of the present invention uses the same solution for an electrolyte solution in an electrolysis cell and an acidic solution in a reservoir, and transports or circulates each of the solutions with each other through a path connecting the electrolysis cell and the reservoir, so that changes in pH of the reservoir and the electrolysis solution may be suppressed, and at the same time, cations may be constantly replenished to the electrolyte solution to maintain ion balance, which may allow the electrolysis to be operated for a long period of time.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011]

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

FIG. 2 is a schematic diagram of a typical carbon dioxide electrolysis device.

(a) of FIG. 3 is a graph showing changes in pH of an electrolyte solution over time in each of Example 1, Comparative Example 1, and Comparative Example 3, and (b) thereof is a graph showing changes in pH of an electrolyte solution over time in each of Example 2, Comparative Example 2, and Comparative Example 4.

(a) of FIG. 4 is a graph showing changes in ion conductivity of an electrolyte solution over time in each of Example 1, Comparative Example 1, and Comparative Example 3, and (b) thereof is a graph showing changes in ion conductivity

of an electrolyte solution over time in each of Example 2, Comparative Example 2, and Comparative Example 4.

MDOE FOR CARRYING OUT THE INVENTION

[0012] 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.

[0013] 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.

[0014] 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.

[0015] The present invention provides an electrolysis device including an electrolysis cell having a gas diffusion layer, a cathode 13, a cation separation membrane 15, an anode 11, and an electrolyte solution, and outside the electrolysis cell, a reservoir 2 connected to a discharge flow path 30 for discharging a product from the cathode, wherein an acidic solution contained in the reservoir 2 and the electrolyte solution are homogeneous solutions.

[0016] 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 device capable of producing useful chemical materials through electrochemical conversion, such as carbon dioxide electrolysis or water electrolysis, or a device which may be utilized for reducing and converting carbon dioxide and NO_x. Specifically, the electrolysis device may be an electrochemical conversion device which converts carbon dioxide into carbon monoxide and ethylene.

[0017] As described in the background art, a typical 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 (HCO₃⁻), 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, resistance increased due to the acidic electrolyte solution, which creates an additional problem in which a voltage increases when driving the typical electrolysis cell. In addition, as a separation membrane to be included in the typical 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. Therefore, the inventor of the present invention developed an electrolysis device of the present invention in which a produced carbonate is not diffused into an anode, and carbon dioxide is separated again from the carbonate, thereby reducing the loss of supplied carbon dioxide.

[0018] According to an embodiment of the present invention, the electrolysis device according to the present invention includes an electrolysis cell and a reservoir 2 connected to the discharge flow path 30 outside the electrolysis cell. The electrolysis cell 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, when the separation membrane 15 is a cation exchange membrane, and if the separation membrane 15 is a cation exchange membrane, the produced carbonate may be prevented from being transported toward the anode 11.

[0019] According to an embodiment of the present invention, the cathode 13 is connected to a supply flow path 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] The reservoir 2 is disposed outside the electrolysis cell, and may be connected to the discharge flow path 30. In addition, the reservoir 2 may contain an acidic solution. The acidic solution may include an aqueous solution containing one or more selected from the group consisting of sulfuric acid, phosphoric acid, hydrochloric acid, nitric acid, acetic acid, citric acid, and oxalic acid, and a salt including one or more selected from the group consisting of cesium, potassium, and sodium. For example, the acidic solution may be a mixed solution containing sulfuric acid (H₂SO₄) and cesium sulfate (Cs₂SO₄). In addition, the salt may include one or more selected from the group consisting of Cs₂CO₃, CsHCO₃, Cs₂SO₄, CsCl, CsNO₃, K₂CO₃, KHCO₃, K₂SO₄, K₃PO₄, KCl, KNO₃, Na₂CO₃, NaHCO₃, Na₂SO₄, Na₃PO₄, NaCl, and NaNO₃.

Carbon dioxide may be separated again from the carbonate by the acidic solution filled in the reservoir 2. That is, the acidic solution may serve to produce carbon dioxide by reacting with a produced carbonate, and specifically, hydrogen ions (H^+) of the acidic solution and a carbonate (HCO_3^-) may react to each other to produce water and carbon dioxide.

[0021] In addition, according to an embodiment of the present invention, the acidic solution of the present invention may be a solution homogeneous with the electrolyte solution. In this case, the acidic solution and the electrolyte solution may be, for example, a mixed solution containing sulfuric acid (H_2SO_4) and cesium sulfate (CS_2SO_4).

[0022] FIG. 2 is a schematic diagram of a typical carbon dioxide electrolysis device. Referring to FIG. 2, in the typical carbon dioxide electrolysis device, a discharge flow path 30-1 of a cathode 13-1 is connected to an acid solution reservoir 20-1. Water and carbon dioxide may be separated from a carbonate by an acidic solution of the acid solution reservoir 20-1, but in this case, the acidic solution is continuously consumed, so that it is difficult for a reaction of the carbonate and hydrogen ions of the acidic solution to continue for a long period of time, and as a result, it may be difficult to achieve continuous driving while maintaining high electrolysis efficiency. Accordingly, the present invention forms a structure in which the acidic solution is homogeneous with the electrolyte solution and the solutions are circulated with each other, so that an acidic solution may be supplied from the electrolyte solution to allow a carbonate reaction to continuously occur in an acid solution reservoir.

[0023] In addition, according to an embodiment of the present invention, the reservoir 2 of the present invention may include an acid solution storage 20 and an electrolyte solution storage 22 connected thereto, and the electrolyte solution storage 22 may be connected to the anode 11 through a solution exchange flow path. The electrolyte solution storage 22 may be spaced apart from the acid solution storage 20, and may be connected to each other through a connector 21. There is a risk that a product in a gaseous state transported from the cathode, for example, carbon monoxide, ethylene, or the like, may be mixed with the acidic solution in the reservoir 2 and not be completely discharged to the outside, and there is a concern that the yield of the product may decrease. In order to prevent the above, the electrolysis device of the present invention includes the reservoir 2 divided into the acid solution storage 20 and the electrolyte solution storage 22, and allows an acidic solution to move between the acid solution storage 20 and the electrolyte solution storage 22 through the connector 21, thereby obtaining a desired level of product yield and facilitating the transport of the acidic solution to an anode through the solution exchange flow path. A solution contained in the electrolyte solution storage 22 may be the same solution as the acidic solution contained in the acid solution storage 20, and the electrolyte solution.

[0024] FIG. 1 is a schematic diagram of a carbon dioxide electrolysis device according to the present invention. Referring to FIG. 1, the acid solution storage 20 may be connected to the cathode 13 by the discharge flow path 30, and the acid solution storage 20 may be connected to the electrolyte solution storage 22 through the connector 21 and disposed spaced apart. In addition, the electrolyte solution storage 22 may be connected to the anode 11 through a solution exchange flow path. In the acid solution storage 20, a carbonate transported from the cathode 13 through the discharge flow path 30 reacts with hydrogen ions of an acidic solution, and carbon dioxide separated thereby and unreacted carbon dioxide may be introduced again into the electrolysis cell through the supply flow path of the cathode 13. In addition, a product transported through the discharge flow path 30 from the cathode 13 to the acid solution storage 20 may be obtained by being discharged to the outside of the electrolysis device from the acid solution storage 20 through a product discharger. At this time, there is a risk that the separated carbon dioxide, the unreacted carbon dioxide, and the product, as materials in a gaseous state, may be mixed with the acidic solution and be introduced into the electrolyte solution storage 22 without being discharged to the outside of the reservoir 2. In order to prevent the above, the position of the product discharger through which a product is discharged to the outside may be set to be higher than the position of the connector 21, and the acidic solution may be filled up to the top of the connector 21 to efficiently discharge the materials in a gaseous state to the outside. The product discharger may serve to discharge the materials in a gaseous state in the acid solution storage 20 to the outside, and the connector 21 may serve to connect the acid solution storage 20 and the electrolyte solution storage 22 to transport the acidic solution. For example, as shown in FIG. 1, the acid solution storage 20, the connector 21, and the electrolyte solution storage 22 may be disposed in an "H" shape.

[0025] In addition, according to an embodiment of the present invention, the solution exchange flow path may include a solution exchange first flow path 40 for transporting the acidic solution from the electrolyte solution storage 22 to the anode 11, and a solution exchange second flow path 50 for transporting an electrolyte solution from the anode 11 to the electrolyte solution storage 22.

[0026] The acidic solution contained in the electrolyte solution storage 22 may be transported to the anode 11 through the solution exchange first flow path 40. In the case of a typical electrolysis device, as an electrolysis reaction proceeds, one or more cations selected from the group consisting of cesium, potassium, and sodium contained in an electrolyte solution moves toward a cathode by a voltage applied to an electrolysis cell, and as a result, cations of the electrolyte solution may be continuously consumed. In addition, the concentration of hydrogen ions relative to the cations of the electrolyte solution increases, thereby lowering the pH of the electrolyte solution, and in this case, a hydrogen production reaction, which is a competitive reaction with a carbon dioxide production reaction, occurs more actively, which may degrade carbon dioxide production efficiency and make long-term driving impossible. In the case of the electrolysis device of the present invention, since the acidic solution and the electrolyte solution correspond to homogeneous solutions, the

cations are supplied to the anode 11 through the solution exchange first flow path 40, and the pH and ion conductivity of the electrolyte solution are maintained at a level similar to that at the beginning of the driving, so that the electrolysis device may be continuously driven.

[0027] In addition, the electrolyte solution may be transported from the anode 11 to the electrolyte solution storage 22 through the solution exchange second flow path 50. As described above, since an acidic solution of the acidic solution storage reacts with a carbonate and separates carbon dioxide, and accordingly, the acidic solution is continuously consumed, the pH in the acidic solution storage gradually increases, so that the acidic solution storage cannot perform its function when a predetermined driving time elapses. In the case of the electrolysis device of the present invention, since the acidic solution and the electrolyte solution correspond to homogeneous solutions, an electrolyte solution is supplied to the electrolyte solution storage 22 from the anode through the solution exchange second flow path 50, and the electrolyte solution is transported from the electrolyte solution storage to the acid solution storage to maintain the pH of the acidic solution in the reservoir 2, so that continuous driving may be achieved. In this case, since a material transported from the anode 11 through the solution exchange second flow path may include not only the electrolyte solution but also an oxygen gas by an oxidation reaction, the solution exchange second flow path 50 may further include a gas-liquid separator 60, wherein a material in a gaseous state may be separated through the gas-liquid separator, and only the electrolyte solution may be transported.

[0028] That is, since the electrolysis device of the present invention is configured to use a homogeneous solution for an electrolyte solution in an electrolysis cell and an acidic solution in an acid solution storage, and at the same time, to transport or circulate the solutions with each other through the solution exchange flow path, the overall ion balance of the electrolysis device may be maintained at a level the same as that at the beginning of the driving, and the electrolysis device may be driven for a long period of time without degradation in electrolysis efficiency.

[0029] According to an embodiment of the present invention, the electrolyte solution may be an aqueous solution containing one or more cations (Na^+ , K^+ , or Cs^+) selected from the group consisting of cesium, potassium, and sodium. In an embodiment, the electrolyte solution may include an aqueous solution containing one or more selected from the group consisting of sulfuric acid, phosphoric acid, hydrochloric acid, nitric acid, acetic acid, citric acid, and oxalic acid, and 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 . In addition, as described above, the electrolyte solution and the acidic solution in the acidic solution storage 20 may be homogeneous solutions.

[0030] According to an embodiment of the present invention, the separation membrane 15 is a cation exchange membrane, 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. Meanwhile, if the separation membrane 15 is an anion exchange membrane, a carbonate is diffused toward an anode, so that the transport of the carbonate to the acid solution storage is not facilitated, which may degrade overall electrolysis efficiency, and may increase the loss of supplied carbon dioxide.

[0031] 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.

[0032] 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.

[0033] Specifically, 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 electrolysis cell having a structure of the 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, thereby minimizing 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, increase the efficiency of a current, and lower overvoltage by solving an additional problem in which a voltage increases during an electrolysis reaction. In addition, in this case, separation plates may be disposed on both sides of the zero-gap membrane electrode assembly to form one cell.

[0034] According to an embodiment of the present invention, a product produced in the cathode 13 by an electrolysis reaction may be transported to the reservoir 2 through the discharge flow path 30, and the product may include carbon monoxide, water vapor, and a salt. The salt may be a carbonate. The carbon dioxide reproduced by separating carbon

dioxide from a carbonate in the acid solution storage 20 may be supplied back to the cathode 13 through a supply flow path. The electrolysis device of the present invention separates carbon dioxide from a carbonate by means of the reservoir 2, and circulates the carbon dioxide into the electrolysis cell to reduce the loss of carbon dioxide, and to increase electrolysis efficiency. In addition, by using a homogeneous solution for an acidic solution and an electrolyte solution, supplying the electrolyte solution to the reservoir 2, and supplying cations of the reservoir 2 to the electrolyte solution, it is possible to achieve long-term driving, and to maintain high electrolysis efficiency.

[0035] Hereinafter, the decomposition principle of the electrolysis device and each component of the electrolysis device will be described.

[0036] 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.

[0037] 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.

[0038] 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_2O_5 , IrO_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).

[0039] 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).

[0040] 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^+).

[0041] 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 sulfate. 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.

[0042] 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.

[0043] 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.

[0044] 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

[0045] The carbon dioxide electrolysis device shown in the schematic diagram of FIG. 1 was operated under operating conditions described below. 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 (0.5 M Cs₂SO₄ pH adjusted to 2 to 3 by H₂SO₄). Solution exchange first and second flow paths were installed to allow the acidic solution and an electrolyte solution to circulate.

Reaction current density: 100 mA/cm² (constant current operation)

Reaction voltage: 1 V to 4 V

Reaction temperature: 40 °C

Reaction pressure: 1 atm (atmospheric pressure)

Anode catalyst: IrO₂ on Ti mesh

Cathode catalyst: Ag powder

Electrode area: 25 cm²

Gas diffusion layer: Sigracet 39BB

Anode electrolyte solution: 0.5 M Cs₂SO₄ pH adjusted to 2~3 by H₂SO₄ (25 ml/min)

Cathode reactant: 40 °C Humidified CO₂ gas (200 ccm)

40 °C Humidified CO₂ gas supply flow 200 ml/min

Example 2

[0046] A carbon dioxide electrolysis device was operated under the same conditions as in Example 1, except that the reaction current density was 200 mA/cm².

Comparative Example 1

[0047] A carbon dioxide electrolysis device was operated under the same conditions as in Example 1, except that an acid solution reservoir was not included (see Table 1).

Comparative Example 2

[0048] A carbon dioxide electrolysis device was operated under the same conditions as in Example 2, except that an acid solution reservoir was not included (see Table 1).

Comparative Example 3

[0049] A carbon dioxide electrolysis device was operated under the same conditions as in Example 1, except that the carbon dioxide electrolysis device shown in the schematic diagram of FIG. 2 was used instead of the carbon dioxide electrolysis device shown in the schematic diagram of FIG. 1 and conditions were changed to the conditions according to Table 1.

Comparative Example 4

[0050] A carbon dioxide electrolysis device was operated under the same conditions as in Example 2, except that the carbon dioxide electrolysis device shown in the schematic diagram of FIG. 2 was used instead of the carbon dioxide electrolysis device shown in the schematic diagram of FIG. 1 and conditions were changed to the conditions according to Table 1.

[0051] The conditions of Examples and Comparative Examples above are shown in Table 1 below.

[Table 1]

Classificati on	Current density (mA/cm ²)	Whether acid solution reservoir is included (O/X)	Whether acidic solution and electrolyte solution are circulated (O/X)	Acidic solution	Electrolyte solution
Example 1	100	○	○	Cs ₂ SO ₄ + H ₂ SO ₄	Cs ₂ SO ₄ + H ₂ SO ₄
Example 2	200	○	○	Cs ₂ SO ₄ + H ₂ SO ₄	Cs ₂ SO ₄ + H ₂ SO ₄
Comparative Example 1	100	X	X	X	Cs ₂ SO ₄ + H ₂ SO ₄
Comparative Example 2	200	X	X	X	Cs ₂ SO ₄ + H ₂ SO ₄
Comparative Example 3	100	○	X	H ₂ SO ₄	Cs ₂ SO ₄
Comparative Example 4	200	○	X	H ₂ SO ₄	Cs ₂ SO ₄

Experimental Example 1 - Measurement of changes in pH of electrolyte solution

[0052] The carbon dioxide electrolysis device according to each of Examples and Comparative Examples was driven for 8 hours, and the pH over time was measured from before the driving of the electrolysis device to 8 hours into the driving, and the measured values are shown in Table 2. In addition, changes in the initial pH values and the pH values after 8 hours are shown in Table 2.

Experimental Example 2 - Measurement of ion conductivity of electrolyte solution

[0053] The carbon dioxide electrolysis device according to each of Examples and Comparative Examples was driven for 8 hours, and the ion conductivity over time of the electrolyte solution was measured from before the driving of the electrolysis device to 8 hours into the driving. The measured values are shown in Table 3. In addition, changes in the initial ion conductivity values and the ion conductivity values after 8 hours are shown in Table 3.

[Table 2]

Example 1		Example 2		Comparative Example 1		Comparative Example 2		Comparative Example 3		Comparative Example 4	
Durati on (min)	pH	Durati on (min)	pH	Durati on (min)	pH	Durati on (min)	pH	Durati on (min)	pH	Durati on (min)	pH
0 (Initial)	2.58	0 (Initial)	3	0 (Initial)	2.58	0 (Initial)	3	0 (Initial)	2.58	0 (Initial)	3
45	2.47	25	3.09	80	2.1	60	2.37	15	2.5	60	2.43
160	2.51	135	3.06	140	1.98	120	2.18	65	2.14	180	2.16
250	2.52	240	3.02	200	1.93	210	2.1	125	2.14	240	2.08
320	2.51	300	3.07	480 (Final)	1.87	480 (Final)	2.08	180	2.14	310	2.11
390	2.56	390	3.13	-	-	-	-	240	2.12	360	2.11
440	2.58	480 (Final)	3.09	-	-	-	-	480 (Final)	2.05	420	2.11
480 (Final)	2.6	-	-	-	-	-	-	-	-	480 (Final)	2.09
Amount of change	0.02	Amount of change	0.09	Amount of change	0.71	Amount of change	0.92	Amount of change	0.53	Amount of change	0.91

[Table 3]

Example 1		Example 2		Comparativ e Example 1		Comparativ e Example 2		Comparativ e Example 3		Comparativ e Example 4	
Durat ion (min)	Ion condu ctivi ty (μ S/c m)	Durat ion (min)	Ion condu ctivi ty (μ S/c m)	Durat ion (min)	Ion condu ctivi ty (μ S/c m)	Durat ion (min)	Ion condu ctivi ty (μ S/c m)	Durat ion (min)	Ion condu ctivi ty (μ S/c m)	Durat ion (min)	Ion condu ctivi ty (μ S/c m)
0 (Init ial)	11328 2	0 (Init ial)	90521 .5	0 (Init ial)	11328 2	0 (Init ial)	90521 .5	0 (Init ial)	11328 2	0 (Init ial)	90521 .5
45	12219 0	25	10272 7	80	15978 3	60	12966 0	15	11893 1	60	11820 5
160	11429 4	135	93052 .5	140	20407 4	120	20534 0	125	16860 8	180	25759 9
250	11352 7	240	10268 5	200	27542 0	210	29330 6	180	24299 5	240	30593 4
320	11776 9	300	10182 4	480 (F inal)	34764 3	480 (Fina 1)	35694 4	240	30072 8	310	31402 1
390	11775 22	390	97303 .4	-	-	-	-	480 (F inal)	37226 2	360	34257 3
440	11703 3	480 (F inal)	91940 .6	-	-	-	-	-	-	420	36535 9
480 (F inal)	11656 5	-	-	-	-	-	-	-	-	480 (Fina 1)	38239 3
Amount of chang e	3283	Amount of chang e	1419. 1	Amount of chang e	23436 1	Amount of chang e	26642 2.5	Amount of chang e	25898 0	Amount of chang e	29187 1.5

[0054] Referring to Table 2, Table 3, FIG. 3, and FIG. 4, it can be confirmed that Examples 1 and 2 in which the electrolysis devices according to the present invention were driven have very little change in the pH and ion conductivity of the electrolyte solution compared to Comparative Examples. That is, it can be confirmed that Examples 1 and 2 use a homogeneous solution for a solution contained in an acid solution storage and an electrolyte solution, and circulate the solution, so that the overall ion balance in the electrolysis device is maintained at a predetermined level.

[0055] Since cesium ions contained in the electrolyte solution move toward the cathode and a relatively large number of hydrogen ions remain, the pH of the electrolyte solution decreases over time, and the ion conductivity of the electrolyte solution increases by hydrogen ions, which have higher ion conductivity than the cesium ions. However, if the pH of the electrolyte solution decreases and the balance between the cesium ions and the hydrogen ions is disrupted, a hydrogen production reaction, which is a competitive reaction with a carbon dioxide production reaction, occurs more actively, thereby degrading carbon dioxide production efficiency and making long-term driving impossible. In comparison with Example 1, which has the same current density, it can be confirmed that Comparative Examples 1 and 3 show that the pH decreases sharply after 8 hours, and the changes in ionic conductivity of the electrolyte solution are also quite large. In addition, in comparison with Example 2, it can be confirmed that Comparative Examples 2 and 4 also show that the changes in pH and ion conductivity after 8 hours are large. That is, since Comparative Examples 1 to 4 show that the changes in pH and ion conductivity of the electrolyte solution are very large, and the ion balance is disrupted, it is expected that the hydrogen production reaction may occur more actively, and the long-term driving may be difficult to be achieved.

2: Reservoir

11: Anode

13: Cathode

15: Separation membrane

20: Acid solution storage

21: Connector

22: Electrolyte solution storage

30: Discharge flow path

40: Solution exchange first flow path

50: Solution exchange second flow path

60: Gas-liquid separator

11-1: Anode of typical device

13-1: Cathode of typical device

15-1: Separation membrane of typical device

20-1: Acid solution reservoir of typical device

30-1: Discharge flow path of typical device

60-1: Gas-liquid separator of typical device

Claims

1. An electrolysis device comprising:

an electrolysis cell including a gas diffusion layer, a cathode, a cation separation membrane, an anode, and an electrolyte solution; and

outside of the electrolysis cell, a reservoir connected by a discharge flow path for discharging a product from the cathode,

wherein an acidic solution contained in the reservoir and the electrolyte solution contained in the electrolysis cell are homogeneous solutions.

2. The electrolysis device of claim 1, wherein the acidic solution comprises: an aqueous solution containing one or more selected from the group consisting of sulfuric acid, phosphoric acid, hydrochloric acid, nitric acid, acetic acid, citric acid, and oxalic acid; and a salt including one or more selected from the group consisting of cesium, potassium, and sodium.

3. The electrolysis device of claim 2, wherein the salt comprises 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 reservoir comprises an acid solution storage and an electrolyte solution

storage connected to the acid solution storage, wherein the electrolyte solution storage is connected to the anode by a solution exchange flow path.

5. The electrolysis device of claim 4, wherein the solution exchange flow path comprises:

a solution exchange first flow path for transferring an acidic solution from the electrolyte solution storage to the anode; and
a solution exchange second flow path for transferring an electrolyte solution from the anode to the electrolyte solution storage.

6. 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.

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

8. The electrolysis device of claim 7, wherein carbon dioxide produced from the salt in the reservoir is supplied to the electrolysis cell.

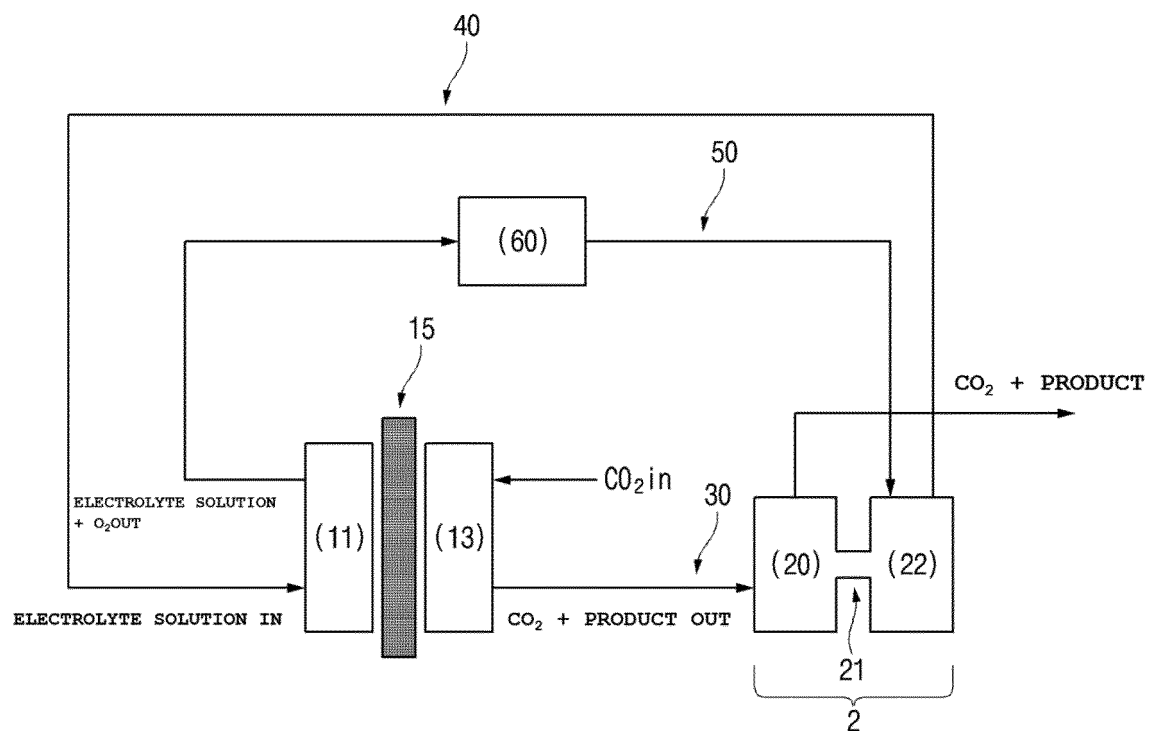
9. The electrolysis device of claim 7, wherein the salt is a carbonate.

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

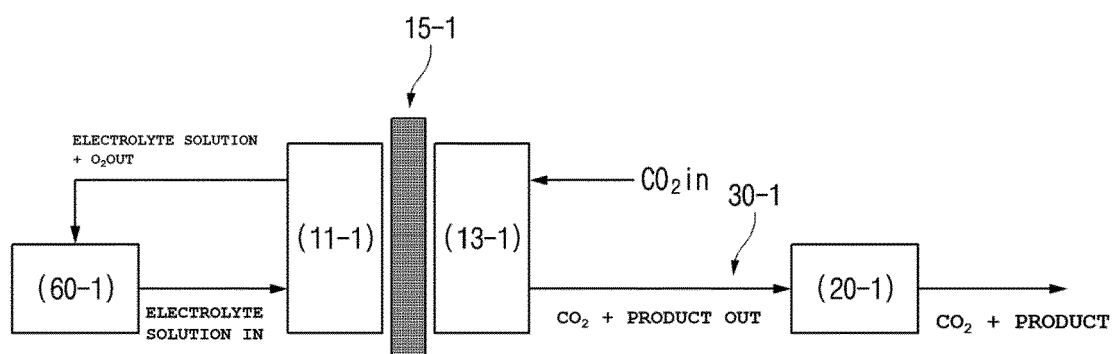
11. The electrolysis device of claim 10, wherein the carbon dioxide is supplied in a state including water vapor when supplied to the electrolysis cell.

12. 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.

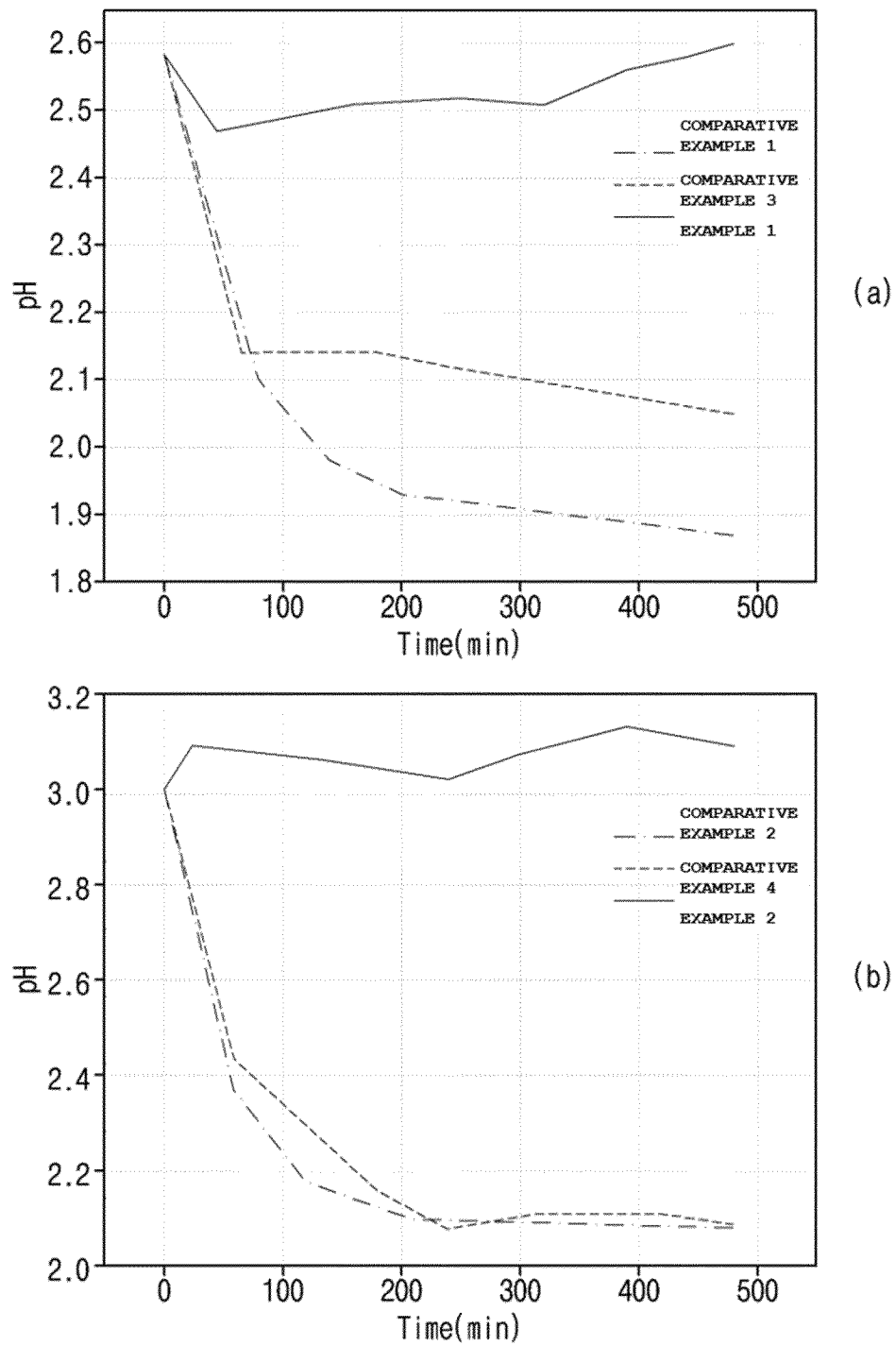
[FIG. 1]



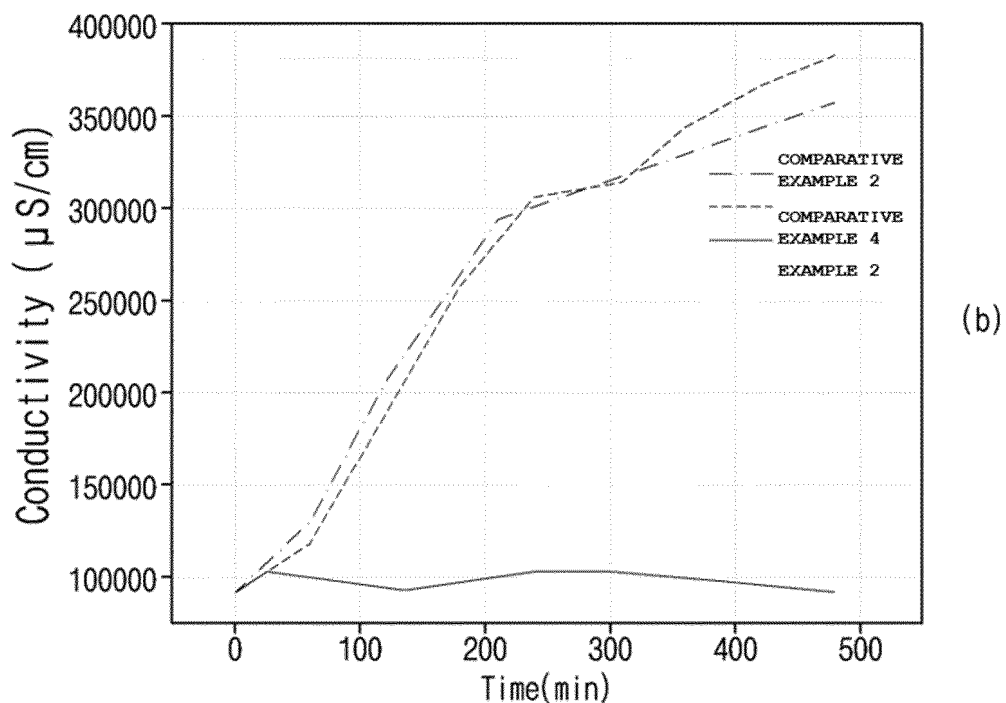
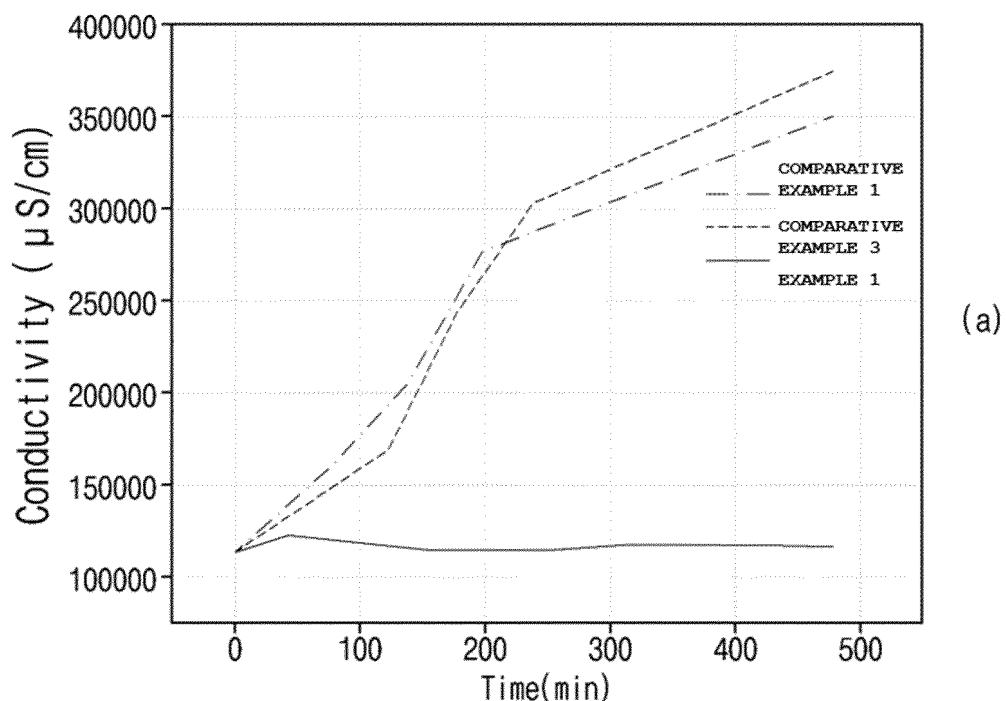
[FIG. 2]



[FIG. 3]



[FIG. 4]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2024/008262

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 11/00(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: 전기 분해(electrolysis), 이산화탄소(carbon dioxide, CO₂), 산성용액(acid solution), 전해액(electrolyte), 탄산염(carbonate), 순환(circulation), 일산화탄소(carbon monoxide, CO), 제로갭(zero gap), 수증기(water vapor)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2022-0079553 A (COVESTRO INTELLECTUAL PROPERTY GMBH & CO. KG) 13 June 2022 (2022-06-13) See claims 1 and 22; paragraphs [0001], [0012], [0074], [0080], [0087], [0092], [0093], [0101]-[0106], [0109] and [0116]; and figures 1 and 2.	1-6,10-12
Y		7-9
Y	KR 10-2021-0086528 A (KOREA INSTITUTE OF ENERGY RESEARCH) 08 July 2021 (2021-07-08) See claims 1 and 5; and paragraph [0003].	7-9
A	KR 10-2017-0117933 A (TECHWIN CO., LTD.) 24 October 2017 (2017-10-24) See claims 1-10; and figures 3a-5b.	1-12
A	KR 10-2015-0055033 A (LIQUID LIGHT, INC.) 20 May 2015 (2015-05-20) See claims 1-30; and figure 1.	1-12



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2024/008262

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

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REFERENCES CITED IN THE DESCRIPTION

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