



(86) **Date de dépôt PCT/PCT Filing Date:** 2012/07/05
 (87) **Date publication PCT/PCT Publication Date:** 2013/01/10
 (85) **Entrée phase nationale/National Entry:** 2013/12/12
 (86) **N° demande PCT/PCT Application No.:** US 2012/045576
 (87) **N° publication PCT/PCT Publication No.:** 2013/006710
 (30) **Priorités/Priorities:** 2011/07/06 (US61/504,828);
 2012/07/05 (US13/541,933)

(51) **Cl.Int./Int.Cl. C25B 3/04** (2006.01),
C25B 9/06 (2006.01)
 (71) **Demandeur/Applicant:**
 LIQUID LIGHT, INC., US
 (72) **Inventeurs/Inventors:**
 LAKKARAJU, PRASAD, US;
 TEAMEY, KYLE, US
 (74) **Agent:** BENNETT JONES LLP

(54) **Titre : CAPTAGE DE DIOXYDE DE CARBONE ET CONVERSION EN PRODUITS ORGANIQUES**
 (54) **Title: CARBON DIOXIDE CAPTURE AND CONVERSION TO ORGANIC PRODUCTS**

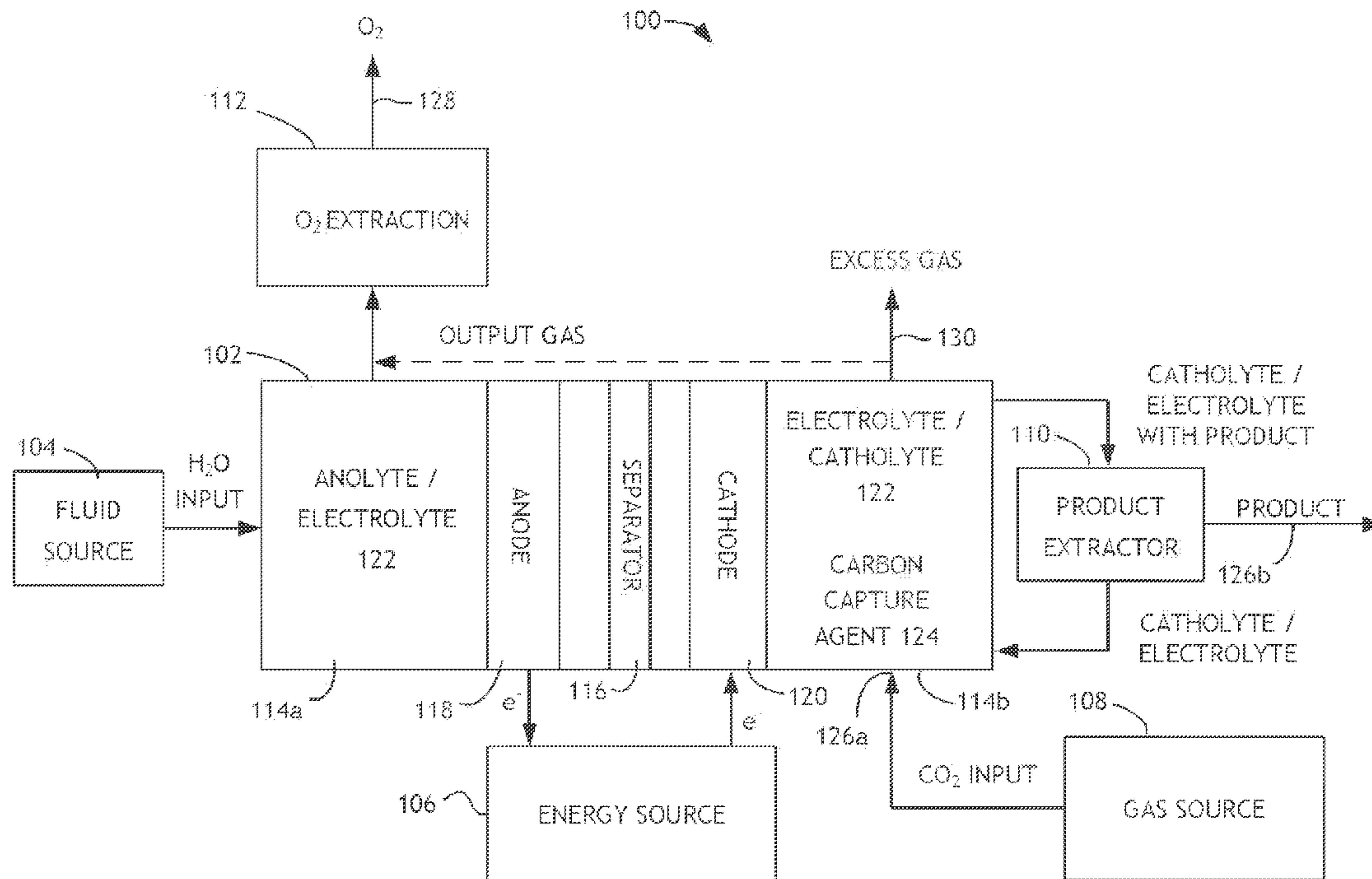


FIG. 1A

(57) **Abrégé/Abstract:**

Methods and systems for capture of carbon dioxide and electrochemical conversion of the captured carbon dioxide to organic products are disclosed. A method may include, but is not limited to, steps (A) to (C). Step (A) may introduce a solvent to a first compartment of an electrochemical cell. Step (B) may capture carbon dioxide with at least one of guanidine, a guanidine derivative, pyrimidine, or a pyrimidine derivative to form a carbamic zwitterion. Step (C) may apply an electrical potential between an anode and a cathode sufficient for the cathode to reduce the carbamic zwitterion to a product mixture.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau(43) International Publication Date
10 January 2013 (10.01.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/006710 A2

- (51) **International Patent Classification:**
C25B 3/04 (2006.01) C25B 9/06 (2006.01)
- (21) **International Application Number:**
PCT/US2012/045576
- (22) **International Filing Date:**
5 July 2012 (05.07.2012)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
61/504,828 6 July 2011 (06.07.2011) US
13/541,933 5 July 2012 (05.07.2012) US
- (71) **Applicant (for all designated States except US):** LIQUID LIGHT, INC. [US/US]; 7 Deer Park Drive, Suite F, Monmouth Junction, NJ 08852 (US).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** LAKKARAJU, Prasad [US/US]; 16 Thom Court, East Brunswick, NJ 08816 (US). TEAMEY, Kyle [US/US]; 4718 Asbury Place NW, Washington, DC 20016 (US).
- (74) **Agent:** SWANTZ, Chad, W.; Suiter Swantz PC LLO, 14301 FNB Parkway, Suite 220, Omaha, NE 68154-5299 (US).
- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— without international search report and to be republished upon receipt of that report (Rule 48.2(g))

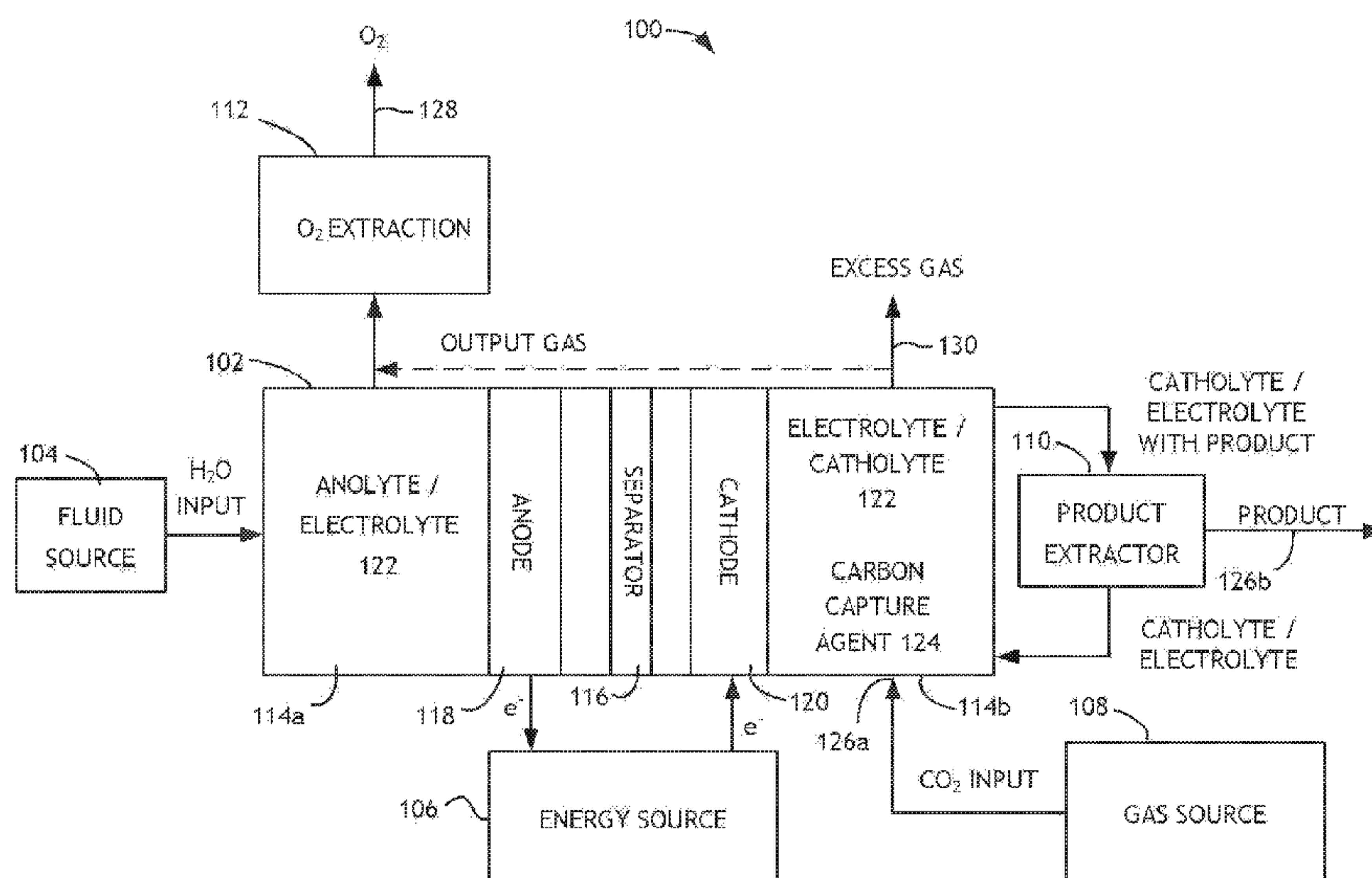
(54) **Title:** CARBON DIOXIDE CAPTURE AND CONVERSION TO ORGANIC PRODUCTS

FIG. 1A

(57) **Abstract:** Methods and systems for capture of carbon dioxide and electrochemical conversion of the captured carbon dioxide to organic products are disclosed. A method may include, but is not limited to, steps (A) to (C). Step (A) may introduce a solvent to a first compartment of an electrochemical cell. Step (B) may capture carbon dioxide with at least one of guanidine, a guanidine derivative, pyrimidine, or a pyrimidine derivative to form a carbamic zwitterion. Step (C) may apply an electrical potential between an anode and a cathode sufficient for the cathode to reduce the carbamic zwitterion to a product mixture.

WO 2013/006710 A2

CARBON DIOXIDE CAPTURE AND CONVERSION TO ORGANIC PRODUCTS

FIELD

[0001] The present disclosure generally relates to the field of
5 electrochemical reactions, and more particularly to methods and/or
systems for capturing carbon dioxide and for electrochemical conversion
of the captured carbon dioxide to organic products.

BACKGROUND

10 [0002] The combustion of fossil fuels in activities such as electricity
generation, transportation, and manufacturing produces billions of tons
of carbon dioxide annually. Research since the 1970s indicates increasing
concentrations of carbon dioxide in the atmosphere may be responsible
for altering the Earth's climate, changing the pH of the ocean and other
15 potentially damaging effects. Countries around the world, including the
United States, are seeking ways to mitigate emissions of carbon dioxide.

[0003] A mechanism for mitigating emissions is to convert carbon dioxide
into economically valuable materials such as fuels and industrial
20 chemicals. If the carbon dioxide is converted using energy from
renewable sources, both mitigation of carbon dioxide emissions and
conversion of renewable energy into a chemical form that can be stored
for later use may be possible.

SUMMARY OF THE PREFERRED EMBODIMENTS

25 [0004] The present invention is directed to using particular capture
agents, solvents, and/or electrolytes to capture/ bind carbon dioxide
and to reduce the captured carbon dioxide to organic products. The
present invention includes the process, system, and various components
30 thereof.

[0005] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not necessarily restrictive of the disclosure as claimed. The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate an embodiment of the disclosure and together with the general description, serve to explain the principles of the disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0006] The numerous advantages of the present disclosure may be better understood by those skilled in the art by reference to the accompanying figures in which:

FIG. 1A is a block diagram of a preferred system in accordance with an embodiment of the present disclosure;

FIG. 1B is a block diagram of a preferred system in accordance with another embodiment of the present disclosure;

FIG. 2 is a flow diagram of a preferred method of capture of carbon dioxide and electrochemical conversion of the carbon dioxide;

FIG. 3 is a flow diagram of another preferred method of capture of carbon dioxide and electrochemical conversion of the carbon dioxide; and

FIG. 4 is a flow diagram of a further preferred method of capture of carbon dioxide and electrochemical conversion of the carbon dioxide.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0007] Reference will now be made in detail to the presently preferred embodiments of the present disclosure, examples of which are illustrated in the accompanying drawings.

[0008] In accordance with preferred embodiments of the present disclosure, an electrochemical system is provided that captures carbon

dioxide and that converts the captured carbon dioxide to organic products. Use of a carbon dioxide capture agent facilitates the capture process. The capture of carbon dioxide may refer herein to the binding of carbon dioxide by reaction of carbon dioxide with a chemical to form an intermediate. It may also refer to the interaction between carbon dioxide and a chemical to form an adduct. It may further refer to the interaction between carbon dioxide and solvents into which the carbon dioxide is bubbled, where the solvents may absorb carbon dioxide and have enhanced solubility for carbon dioxide than does an aqueous solution.

[0009] Before any embodiments of the invention are explained in detail, it is to be understood that the embodiments described below do not limit the scope of the claims that follow. Also, it is to be understood that the phraseology and terminology used herein is for the purpose of description and should not be regarded as limiting. The use of terms such as "including," "comprising," or "having" and variations thereof herein are generally meant to encompass the item listed thereafter and equivalents thereof as well as additional items. Further, unless otherwise noted, technical terms may be used according to conventional usage.

[0010] In certain preferred embodiments, the capture of carbon dioxide and the reduction of the captured carbon dioxide to produce organic products may be preferably achieved in a divided electrochemical or photoelectrochemical cell having at least two compartments. One compartment contains an anode suitable for oxidation, and another compartment contains a working cathode electrode and a carbon dioxide capture agent. The compartments may be separated by a porous glass frit, microporous separator, ion exchange membrane, or other ion conducting bridge. Both compartments generally contain an aqueous or non-aqueous solution of an electrolyte. Carbon dioxide gas may be continuously bubbled through the cathodic electrolyte solution to

preferably saturate the solution or the solution may be pre-saturated with carbon dioxide. Mixing of carbon dioxide with the electrolyte solution and/or a carbon dioxide capture agent may occur within the cathode chamber or in a mixing chamber external to the cathode chamber.

[0011] Referring to FIG. 1A, a block diagram of a system 100 is shown in accordance with an embodiment of the present invention. System 100 may be utilized for capture of carbon dioxide and conversion of the captured carbon dioxide to organic products. The system (or apparatus) 100 generally comprises a cell (or container) 102, a fluid source 104 (to supply solvent to the cell 102), an energy source 106, a gas source 108, a product extractor 110 and an oxygen extractor 112. A product or product mixture may be output from the product extractor 110 after extraction. An output gas containing oxygen may be output from the oxygen extractor 112 after extraction.

[0012] The cell 102 may be implemented as a divided cell. The divided cell may be a divided electrochemical cell and/or a divided photochemical cell. The cell 102 is generally operational to capture carbon dioxide (CO₂) and to reduce carbon dioxide into products or product intermediates. In particular implementations, the cell 102 is operational to capture carbon dioxide by binding carbon dioxide to a structure and/or molecule and/or by increasing the solubility of carbon dioxide in the solvent. The reduction generally takes place by introducing (e.g., bubbling) carbon dioxide into an electrolyte solution in the cell 102. A carbon dioxide capture agent in the cell may capture at least a portion of the introduced carbon dioxide. In another implementation (as shown in FIG. 1B), the carbon dioxide capture agent and the carbon dioxide interact external to the cathode chamber to permit capture of carbon dioxide prior to introduction to the cathode

chamber. A cathode 120 in the cell 102 may reduce the captured carbon dioxide into a product mixture, where the product mixture preferably includes organic products.

5 [0013] The cell 102 generally comprises two or more compartments (or chambers) 114a-114b, a separator (or membrane) 116, an anode 118, and a cathode 120. The anode 118 may be disposed in a given compartment (e.g., 114a). The cathode 120 may be disposed in another compartment (e.g., 114b) on an opposite side of the separator 116 as the
10 anode 118. In particular implementations, the cathode 120 includes materials suitable for the reduction of carbon dioxide including cadmium, a cadmium alloy, cobalt, a cobalt alloy, nickel, a nickel alloy, chromium, a chromium alloy, indium, an indium alloy, iron, an iron alloy, copper, a copper alloy, lead, a lead alloy, palladium, a palladium
15 alloy, platinum, a platinum alloy, molybdenum, a molybdenum alloy, tungsten, a tungsten alloy, niobium, a niobium alloy, silver, a silver alloy, tin, a tin alloy, rhodium, a rhodium alloy, ruthenium, a ruthenium alloy, carbon, and mixtures thereof. An electrolyte solution 122 (e.g., anolyte or catholyte 122) may fill both compartments 114a-114b. The
20 electrolyte solution 122 may include water as a solvent with water soluble salts for providing various cations and anions in solution, however an organic solvent may also be utilized. A carbon dioxide capture agent 124 is preferably added to the compartment 114b, in certain implementations is also added to the compartment 114a, and in other
25 implementations is added to a mixing chamber 132 (as shown in FIG. 1B) external to the compartment 114b. For instance, the carbon dioxide capture agent 124 may be utilized as the solvent and/or electrolyte for the compartments 114a and 114b of the cell 102.

30 [0014] In a particular implementation, the carbon dioxide capture agent 124 includes at least one of guanidine, a guanidine derivative,

pyrimidine, or a pyrimidine derivative. Preferred guanidine and pyrimidine derivatives include 1,1,3,3 tetramethylguanidine, 1,5,7-triazabicyclo[4.4.0]dec-5-ene, 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,5-diazabicyclo[4.3.0]non-5-ene, and 1,4,5,6-tetrahydropyrimidine. In this implementation, the cell 102 preferably includes an aqueous solvent, a solvent including acetonitrile, dimethylfuran, or another organic solvent, or a mixture of water and an organic solvent (comprising between about 1% and 100% water by volume). The carbon dioxide capture agent 124 may facilitate capture of carbon dioxide in the compartment 114b (or in the mixing chamber 132) by forming a carbamic zwitterion with the carbon dioxide. Upon application of an electric potential between the anode 118 and the cathode 120, the carbamic zwitterion is reduced at the cathode 120, generating an organic product and regenerating the carbon dioxide capture agent. The organic product may include one or more of acetaldehyde, acetate, acetic acid, acetone, 1-butanol, 2-butanol, 2-butanone, carbon, carbon monoxide, carbonates, ethane, ethanol, ethylene, formaldehyde, formate, formic acid, glycolate, glycolic acid, glyoxal, glyoxylic acid, graphite, isopropanol, lactate, lactic acid, methane, methanol, oxalate, oxalic acid, propanal, 1-propanol, and polymers containing carbon dioxide.

[0015] In another particular implementation, the carbon dioxide capture agent is an ionic liquid that includes at least one of a guanidinium-based cation or a pyrimidium-based cation and preferably includes a halide anion, a sulfate anion, a phosphate anion, a nitrate anion, or another anion. The ionic liquid may act as a carbon dioxide capture 124 agent, a solvent, and an electrolyte. The ionic liquid may facilitate capture of the carbon dioxide (in the compartment 114b or in the mixing chamber 132) by increasing the solubility of the carbon dioxide as compared to an aqueous solvent. Upon application of an electric potential between the anode 118 and the cathode 120, the captured carbon dioxide is reduced

at the cathode 120, generating an organic product. The organic product may include one or more of acetaldehyde, acetate, acetic acid, acetone, 1-butanol, 2-butanol, 2-butanone, carbon, carbon monoxide, carbonates, ethane, ethanol, ethylene, formaldehyde, formate, formic acid, glycolate, glycolic acid, glyoxal, glyoxylic acid, graphite, isopropanol, lactate, lactic acid, methane, methanol, oxalate, oxalic acid, propanal, 1-propanol, and polymers containing carbon dioxide.

[0016] In another implementation, the carbon dioxide capture agent 124 includes a non-aqueous, organic solvent. The organic solvent preferably includes one or more of methanol, acetonitrile, and dimethylfuran, and may include other organic solvents, provided that the organic solvent aids in the capture of carbon dioxide, such by including a higher solubility limit for carbon dioxide as compared to an aqueous solvent. The capture of the carbon dioxide may occur in one or more of the compartment 114b and the mixing chamber 132. In this implementation, the cell 102 may include an electrolyte suitable for a non-aqueous solvent, preferably with a quaternary ammonium cation. The electrolyte may include a halide-based anion. The compartment 114b preferably includes a pyridine-based catalyst to facilitate reduction of carbon dioxide at the cathode 120. Upon application of an electric potential between the anode 118 and the cathode 120, the captured carbon dioxide is reduced at the cathode 120, generating an organic product. The organic product may include one or more of carbon monoxide, carbonate, and oxalate.

[0017] The pH of the compartment 114b is preferably between about 1 and 9. A pH range of between about 1 to about 4 is preferable for production of carboxylic acids from carbon dioxide. A pH range of between about 4 to about 9 is preferable for production of other organic products (e.g., carbonates, carboxylates, aldehydes, ketones, alcohols, alkanes, and alkenes) from carbon dioxide. Other pH values may be

utilized, such as when the carbon dioxide capture agent 124 includes an ionic liquid or an organic solvent.

[0018] The fluid source 104 preferably includes a water source, such that
5 the fluid source 104 may provide pure water to the cell 102. The fluid
source 104 may provide other fluids to the cell 102, including an organic
solvent, such as methanol, acetonitrile, and dimethylfuran. The fluid
source 104 may also provide a mixture of an organic solvent and water to
the cell 102. In the implementations where the carbon dioxide capture
10 agent 124 is an ionic liquid, the fluid source 104 may provide the ionic
liquid to the cell 102.

[0019] The energy source 106 may include a variable electrical power
source. The energy source 106 may be operational to generate an
15 electrical potential between the anode 118 and the cathode 120. The
electrical potential may be a DC voltage. In preferred embodiments, the
applied electrical potential is generally between about -0.5V vs. SCE and
about -3V vs. SCE at the cathode, and preferably from about -0.6V vs.
SCE to about -2.5V vs. SCE at the cathode.

20

[0020] The gas source 108 preferably includes a carbon dioxide source. In
some embodiments, carbon dioxide is bubbled directly into the
compartment 114b containing the cathode 120. For instance, the
compartment 114b may include a carbon dioxide input, such as a port
25 126a configured to be coupled between the carbon dioxide source and
the cathode 120. In other preferred embodiments, the carbon dioxide
from the gas source 108 is introduced to the mixing chamber 132, as
shown in FIG. 1B. The carbon capture agent 124 may also be introduced
to the mixing chamber 132. The mixing chamber 132 generally
30 facilitates the interaction between the carbon dioxide and the carbon
capture agent 124 to permit the capture of carbon dioxide within the

mixing chamber 132. In a particular implementation, the mixing chamber 132 includes a stripping column to facilitate interaction between the carbon dioxide and the carbon capture agent 124. The captured carbon dioxide may be introduced to the cathode compartment 5 114b for reduction of the captured carbon dioxide at the cathode 120 to produce a product mixture and to regenerate the carbon capture agent 124.

[0021] Advantageously, the carbon dioxide may be obtained from any 10 source (e.g., an exhaust stream from fossil-fuel burning power or industrial plants, from geothermal or natural gas wells or the atmosphere itself). Most suitably, the carbon dioxide may be obtained from concentrated point sources of generation prior to being released into the atmosphere. For example, high concentration carbon dioxide 15 sources may frequently accompany natural gas in amounts of 5% to 50%, exist in flue gases of fossil fuel (e.g., coal, natural gas, oil, etc.) burning power plants, and high purity carbon dioxide may be exhausted from cement factories, from fermenters used for industrial fermentation of ethanol, and from the manufacture of fertilizers and refined oil 20 products. Certain geothermal steams may also contain significant amounts of carbon dioxide. The carbon dioxide emissions from varied industries, including geothermal wells, may be captured on-site. Thus, the capture and use of existing atmospheric carbon dioxide in accordance with some embodiments of the present invention generally 25 allow the carbon dioxide to be a renewable and essentially unlimited source of carbon.

[0022] The product extractor 110 may include an organic product and/or inorganic product extractor. The product extractor 110 generally 30 facilitates extraction of one or more products from the electrolyte 122 and/or the carbon dioxide capture agent 124. The extraction may occur via one or more of a solid sorbent, carbon dioxide-assisted solid sorbent,

liquid-liquid extraction, nanofiltration, and electrodialysis. The extracted products may be presented through a port 126b of the system 100 for subsequent storage, consumption, and/or processing by other devices and/or processes. In particular implementations, the product is
5 continuously removed from the cell 102, where cell 102 operates on a continuous basis, such as through a continuous flow-single pass reactor where fresh catholyte and carbon dioxide is fed continuously as the input, and where the output from the reactor is continuously removed. The carbon dioxide capture agent 124 may be recycled back into the
10 compartment 114b for capture of additional carbon dioxide.

[0023] The oxygen extractor 112 of FIG. 1 is generally operational to extract oxygen (e.g., O₂) byproducts created by the reduction of the carbon dioxide and/or the oxidation of water. In preferred
15 embodiments, the oxygen extractor 112 is a disengager/flash tank. The extracted oxygen may be presented through a port 128 of the system 100 for subsequent storage and/or consumption by other devices and/or processes. Chlorine and/or oxidatively evolved chemicals may also be byproducts in some configurations, such as in an embodiment of
20 processes other than oxygen evolution occurring at the anode 118. Such processes may include chlorine evolution, oxidation of organics to other saleable products, waste water cleanup, and corrosion of a sacrificial anode. Any other excess gases (e.g., hydrogen) created by the reduction of the carbon dioxide may be vented from the cell 102 via a port 130.

25
[0024] Referring to FIG. 2, a flow diagram of a preferred method 200 for capture of carbon dioxide and electrochemical conversion of the carbon dioxide is shown. The method (or process) 200 generally comprises a step (or block) 202, a step (or block) 204, and a step (or block) 206. The
30 method 200 may be implemented using the system 100.

[0025] In the step 202, a solvent may be introduced to a first compartment of an electrochemical cell. The first compartment may include an anode. The electrochemical cell may also include a second compartment containing a cathode. Capturing carbon dioxide with at least one of guanidine, a guanidine derivative, pyrimidine, or a pyrimidine derivative may be performed in the step 204. In the step 206, an electrical potential may be applied between the anode and the cathode sufficient for the cathode to reduce the carbamic zwitterion to a product mixture. The product mixture may include one or more of acetaldehyde, acetate, acetic acid, acetone, 1-butanol, 2-butanol, 2-butanone, carbon, carbon monoxide, carbonates, ethane, ethanol, ethylene, formaldehyde, formate, formic acid, glycolate, glycolic acid, glyoxal, glyoxylic acid, graphite, isopropanol, lactate, lactic acid, methane, methanol, oxalate, oxalic acid, propanal, 1-propanol, and polymers containing carbon dioxide.

[0026] Referring to FIG. 3, a flow diagram of another preferred method 300 for capture of carbon dioxide and electrochemical conversion of the carbon dioxide is shown. The method (or process) 300 generally comprises a step (or block) 302, a step (or block) 304, and a step (or block) 306. The method 300 may be implemented using the system 100.

[0027] In the step 302, an ionic liquid may be introduced to at least one of a cathode compartment of an electrochemical cell or a mixing chamber. The ionic liquid may comprise at least one of a guanidinium-based cation or a pyrimidium-based cation. The electrochemical cell may include an anode in an anode compartment and may include a cathode in the cathode compartment. Capturing carbon dioxide with the ionic liquid may be performed in the step 304. The second compartment may include a cathode. In the step 306, an electrical potential may be applied between the anode and the cathode sufficient for the cathode to reduce the captured carbon dioxide to a product mixture. The product

mixture may include one or more of acetaldehyde, acetate, acetic acid, acetone, 1-butanol, 2-butanol, 2-butanone, carbon, carbon monoxide, carbonates, ethane, ethanol, ethylene, formaldehyde, formate, formic acid, glycolate, glycolic acid, glyoxal, glyoxylic acid, graphite, isopropanol, lactate, lactic acid, methane, methanol, oxalate, oxalic acid, propanal, 1-propanol, and polymers containing carbon dioxide.

[0028] Referring to FIG. 4, a flow diagram of another preferred method 400 for capture of carbon dioxide and electrochemical conversion of the carbon dioxide is shown. The method (or process) 400 generally comprises a step (or block) 402, a step (or block) 404, and a step (or block) 406. The method 400 may be implemented using the system 100.

[0029] In the step 402, a carbon dioxide capture agent may be introduced to at least one of a cathode compartment of an electrochemical cell or a mixing chamber. The carbon dioxide capture agent may comprise an organic solvent. The electrochemical cell may include an anode in an anode compartment and may include a cathode and a pyridine-based catalyst in the cathode compartment. Capturing carbon dioxide with the carbon dioxide capture agent may be performed in the step 404. The second compartment may include a cathode and a pyridine-based catalyst. In the step 406, an electrical potential may be applied between the anode and the cathode sufficient for the cathode to reduce the captured carbon dioxide to a product mixture. The product mixture may include one or more of carbon monoxide, carbonate, and oxalate.

[0030] It is believed that the present disclosure and many of its attendant advantages will be understood by the foregoing description, and it will be apparent that various changes may be made in the form, construction and arrangement of the components thereof without departing from the scope and spirit of the disclosure or without sacrificing all of its material advantages. The form herein before

described being merely an explanatory embodiment thereof, it is the intention of the following claims to encompass and include such changes.

LL0014 PCT

CLAIMS

What is claimed is:

5 1. A method for electrochemical conversion of carbon dioxide, comprising:

(A) introducing a solvent to a first compartment of an electrochemical cell, the first compartment including an anode, the electrochemical cell including a second compartment containing a cathode;

10 (B) capturing carbon dioxide with at least one of guanidine, a guanidine derivative, pyrimidine, or a pyrimidine derivative to form a carbamic zwitterion; and

(C) applying an electrical potential between the anode and the cathode sufficient for the cathode to reduce the carbamic zwitterion to a
15 product mixture.

2. The method of claim 1, wherein capturing carbon dioxide with at least one of guanidine, a guanidine derivative, pyrimidine, or a pyrimidine derivative to form a carbamic zwitterion includes:

20 capturing carbon dioxide in the second compartment with at least one of guanidine, a guanidine derivative, pyrimidine, or a pyrimidine derivative to form a carbamic zwitterion.

3. The method of claim 1, wherein capturing carbon dioxide with at least one of guanidine, a guanidine derivative, pyrimidine, or a
25 pyrimidine derivative to form a carbamic zwitterion includes:

 capturing carbon dioxide in a mixing chamber with at least one of guanidine, a guanidine derivative, pyrimidine, or a pyrimidine derivative to form a carbamic zwitterion before the captured carbon dioxide is delivered to the second compartment.

LL0014 PCT

4. The method of claim 1, wherein applying an electrical potential between the anode and the cathode sufficient for the cathode to reduce the carbamic zwitterion to a product mixture includes:

5 applying an electrical potential between the anode and the cathode sufficient for the cathode to reduce the carbamic zwitterion to a product mixture and to regenerate the at least one of guanidine, the guanidine derivative, pyrimidine, or the pyrimidine derivative.

10 5. The method of claim 1, wherein the second compartment includes at least one of 1,1,3,3 tetramethylguanidine, 1,5,7-triazabicyclo[4.4.0]dec-5-ene, 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,5-diazabicyclo[4.3.0]non-5-ene, or 1,4,5,6-tetrahydropyrimidine.

15

6. The method of claim 1, wherein the solvent is at least one of water, methanol, acetonitrile, dimethylfuran, or a mixture of water and an organic solvent.

20

LL0014 PCT

7. A system for electrochemical reduction of carbon dioxide, comprising:

an electrochemical cell including:

a first cell compartment;

5 an anode positioned within said first cell compartment;

a second cell compartment;

a cathode positioned within said second cell compartment;

a carbamic zwitterion; and

10 an energy source operably coupled with said anode and said cathode, said energy source configured to apply a voltage between said anode and said cathode to reduce the carbamic zwitterion at said cathode to a product mixture.

8. The system of claim 7, wherein the carbamic zwitterion is
15 formed by interacting carbon dioxide with at least one of guanidine, a guanidine derivative, pyrimidine, or a pyrimidine derivative.

9. The system of claim 8, wherein the carbamic zwitterion is formed at least one of (a) within said second cell compartment or (b) in a
20 mixing chamber prior to introduction to said second cell compartment.

10. The system of claim 7, wherein the energy source is further configured to apply a voltage between said anode and said cathode to regenerate the at least one of guanidine, a guanidine derivative,
25 pyrimidine, or a pyrimidine derivative.

11. The system of claim 7, wherein the second compartment includes at least one of 1,1,3,3 tetramethylguanidine, 1,5,7-triazabicyclo[4.4.0]dec-5-ene, 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-

LL0014 PCT

ene, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,5-diazabicyclo[4.3.0]non-5-ene,
or 1,4,5,6-tetrahydropyrimidine.

5

LL0014 PCT

12. A method for electrochemical conversion of carbon dioxide, comprising:

- (A) introducing an ionic liquid to at least one of a cathode compartment of an electrochemical cell or a mixing chamber, the ionic liquid comprising at least one of a guanidinium-based cation or a pyrimidium-based cation, the electrochemical cell including an anode in an anode compartment and including a cathode in the cathode compartment;
- (B) capturing carbon dioxide with the ionic liquid; and
- (C) applying an electrical potential between the anode and the cathode sufficient for the cathode to reduce the captured carbon dioxide to a product mixture.

13. The method of claim 12, wherein the ionic liquid further comprises at least one of a halide anion, a sulfate anion, a phosphate anion, or a nitrate anion.

14. The method of claim 12, wherein capturing carbon dioxide with the ionic liquid includes:
capturing carbon dioxide in the cathode compartment with the ionic liquid.

15. The method of claim 12, wherein capturing carbon dioxide with the ionic liquid includes:
capturing carbon dioxide in the mixing chamber with the ionic liquid.

16. The method of claim 15, further comprising:
delivering the captured carbon dioxide to the cathode compartment.

LL0014 PCT

17. A method for electrochemical conversion of carbon dioxide, comprising:

(A) introducing a carbon dioxide capture agent to at least one of a cathode compartment of an electrochemical cell or a mixing chamber, the carbon dioxide capture agent comprising an organic solvent, the
5 electrochemical cell including an anode in an anode compartment and including a cathode and a pyridine-based catalyst in the cathode compartment;

(B) capturing carbon dioxide with the carbon dioxide capture
10 agent; and

(C) applying an electrical potential between the anode and the cathode sufficient for the cathode to reduce the captured carbon dioxide to a product mixture.

15 18. The method of claim 17, wherein the organic solvent includes at least one of methanol, acetonitrile, or dimethylfuran.

19. The method of claim 17, wherein capturing carbon dioxide with the carbon dioxide capture agent includes:

20 capturing carbon dioxide in the cathode compartment with the carbon dioxide capture agent.

20. The method of claim 17, wherein capturing carbon dioxide with the carbon dioxide capture agent includes:

25 capturing carbon dioxide in the mixing chamber with the carbon dioxide capture agent.

21. The method of claim 20, further comprising:
delivering the captured carbon dioxide to the cathode compartment.

30

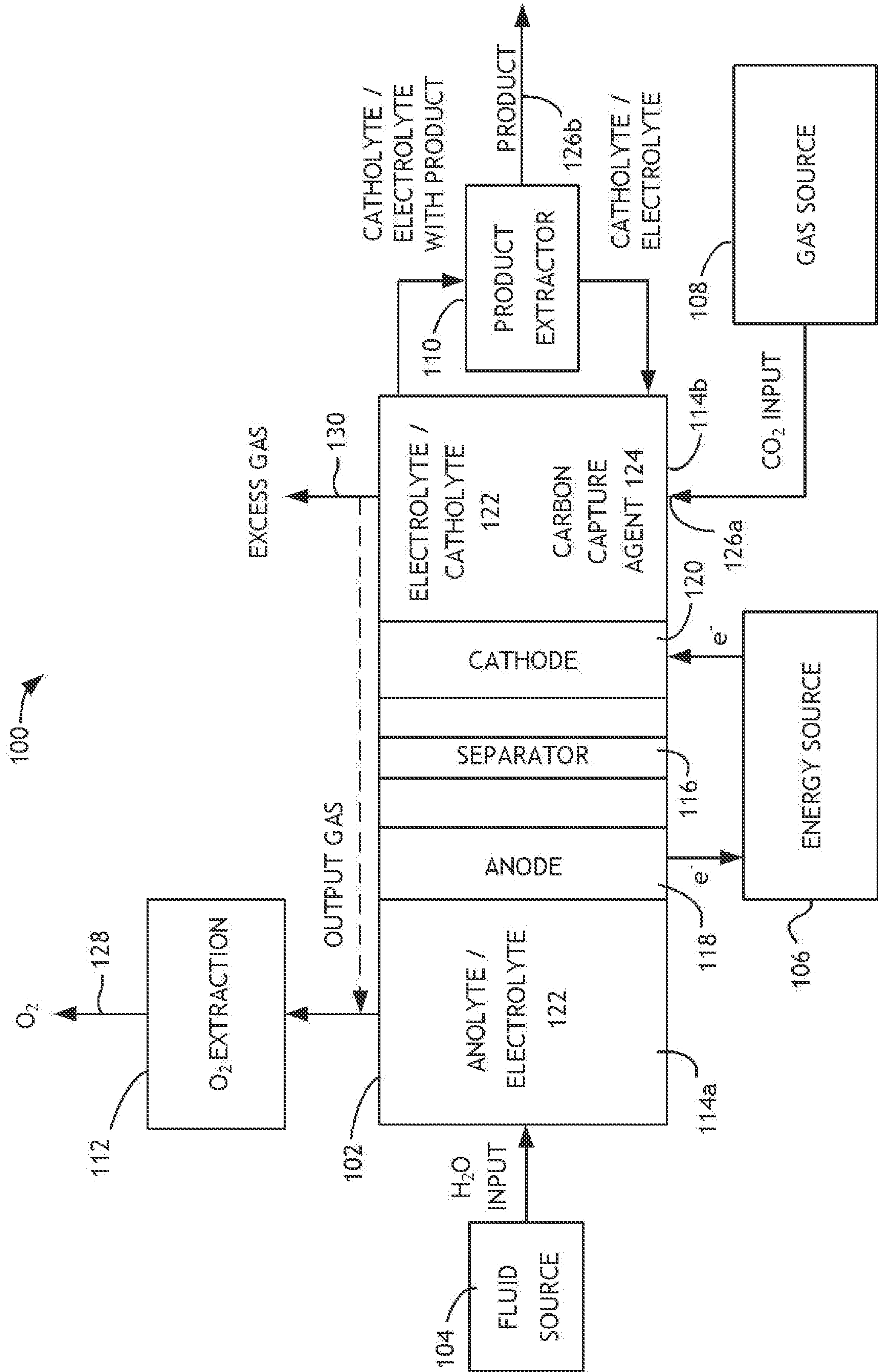


FIG. 1A

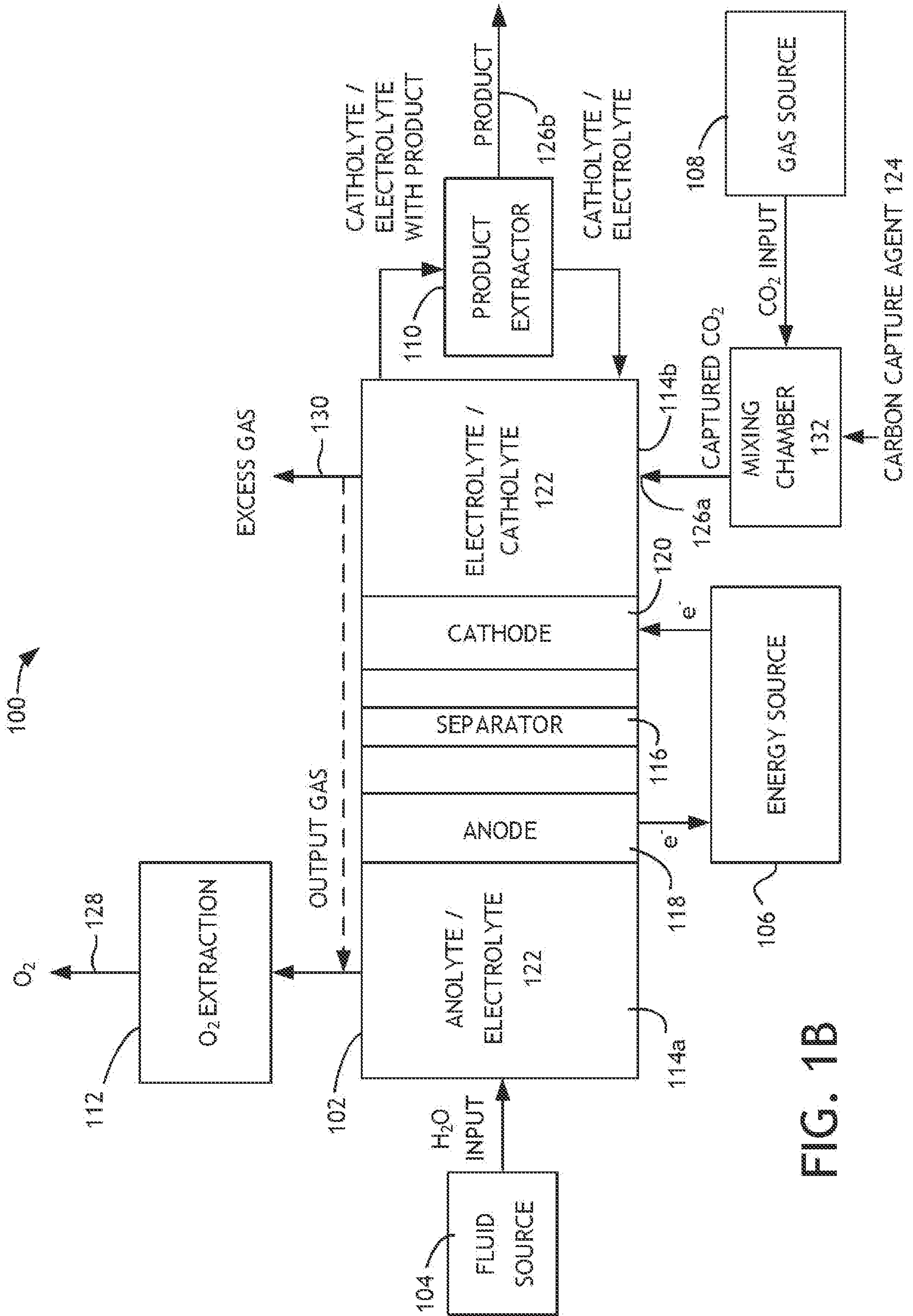


FIG. 1B

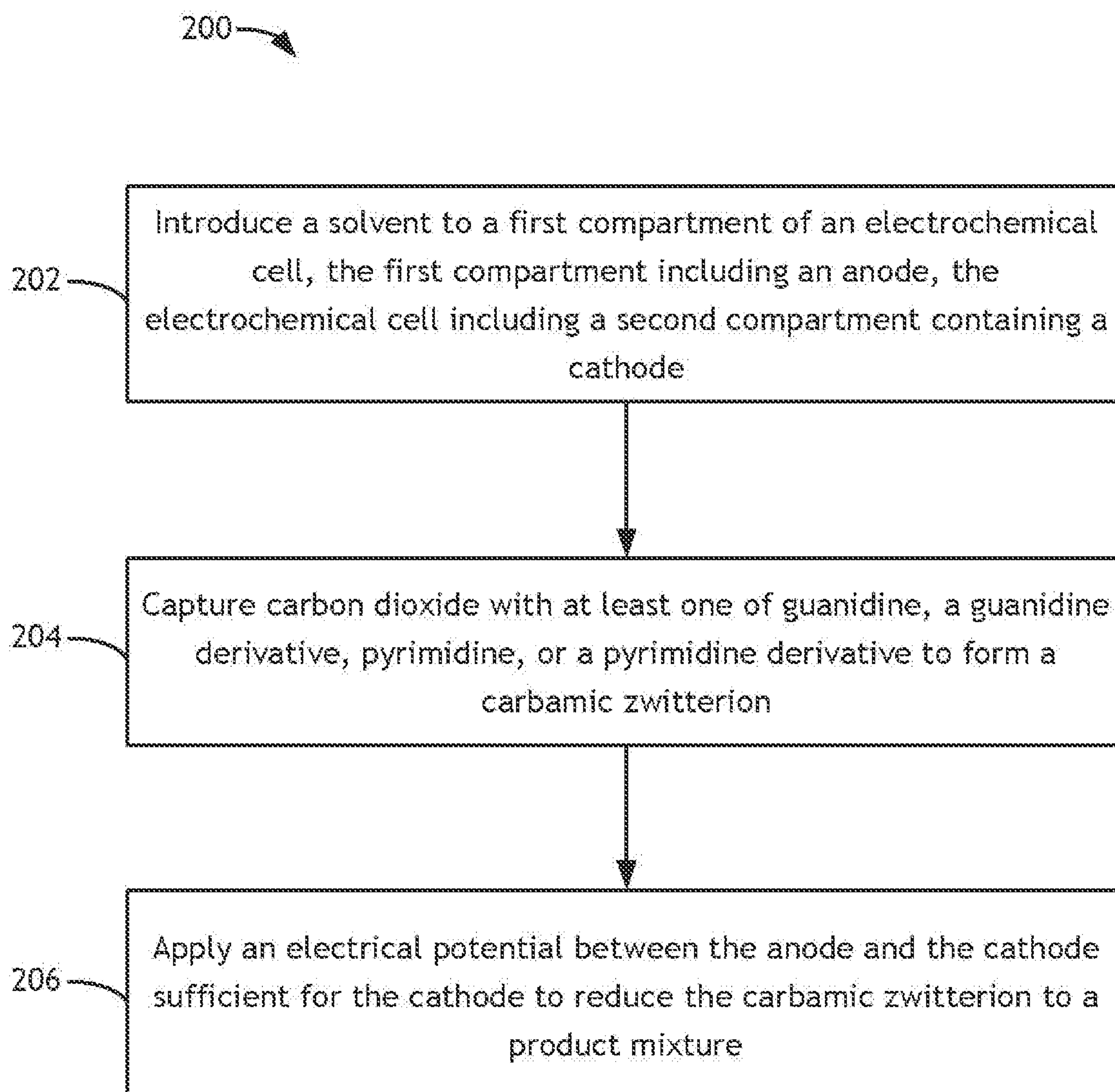


FIG. 2

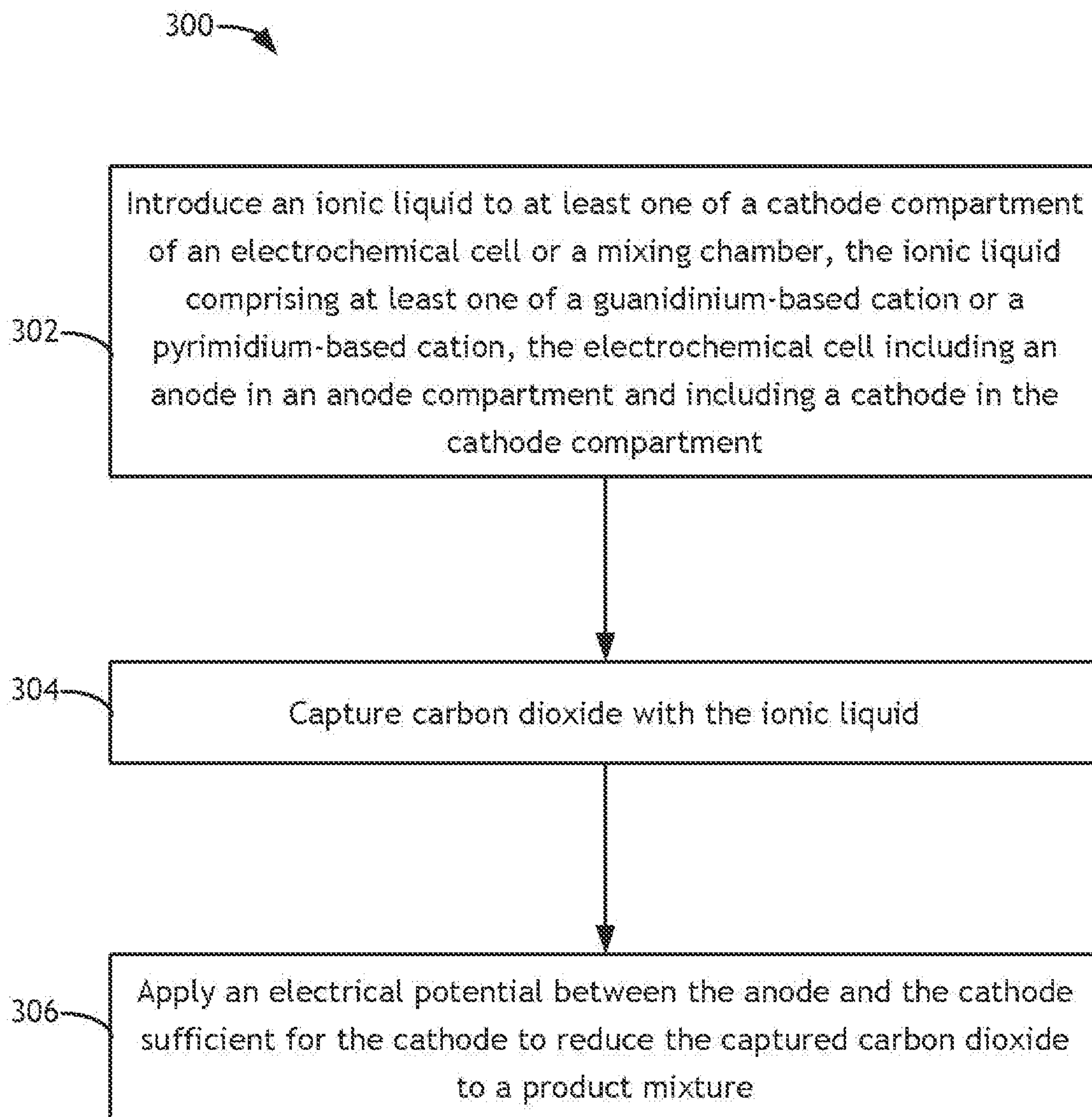


FIG. 3

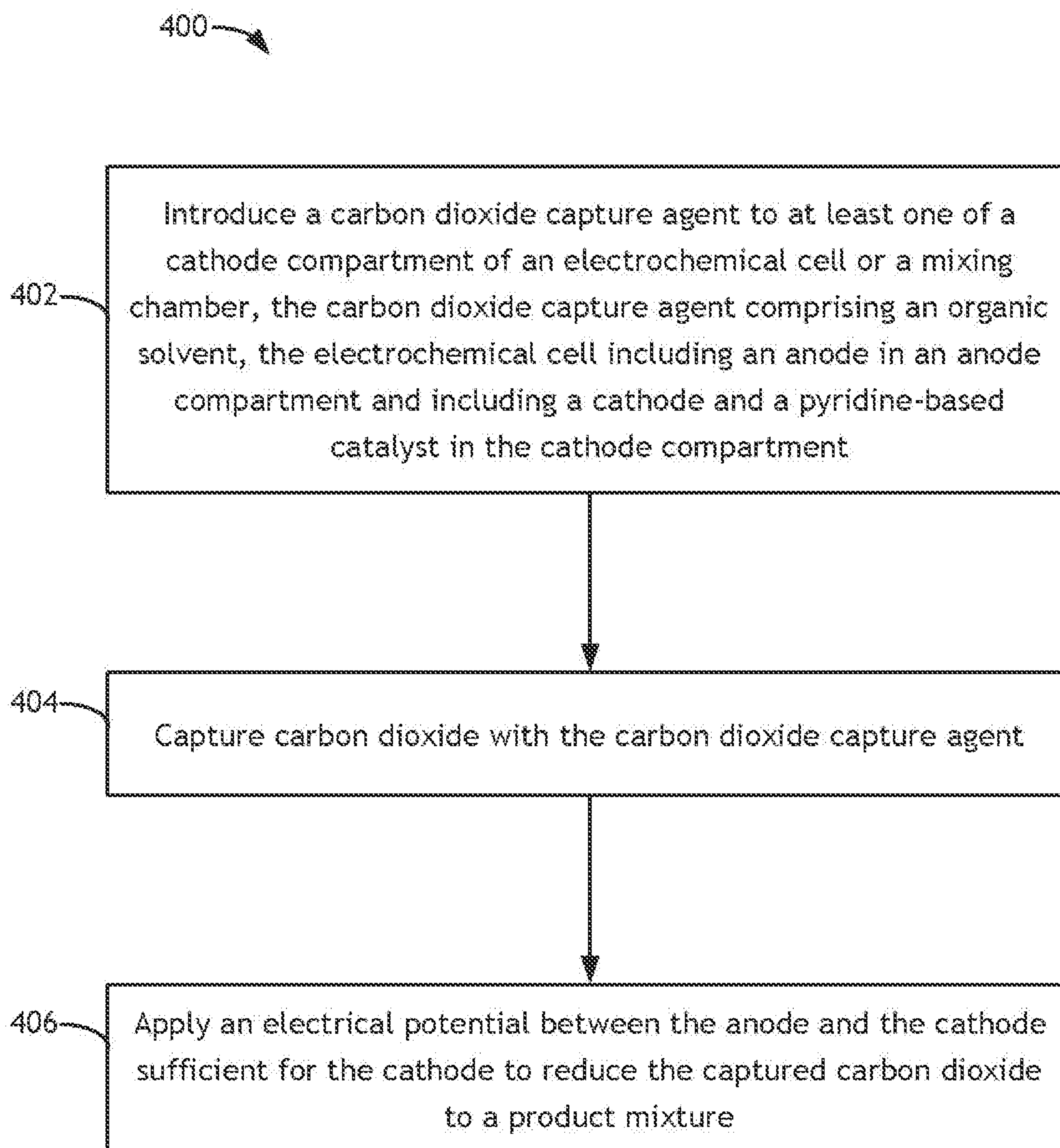


FIG. 4

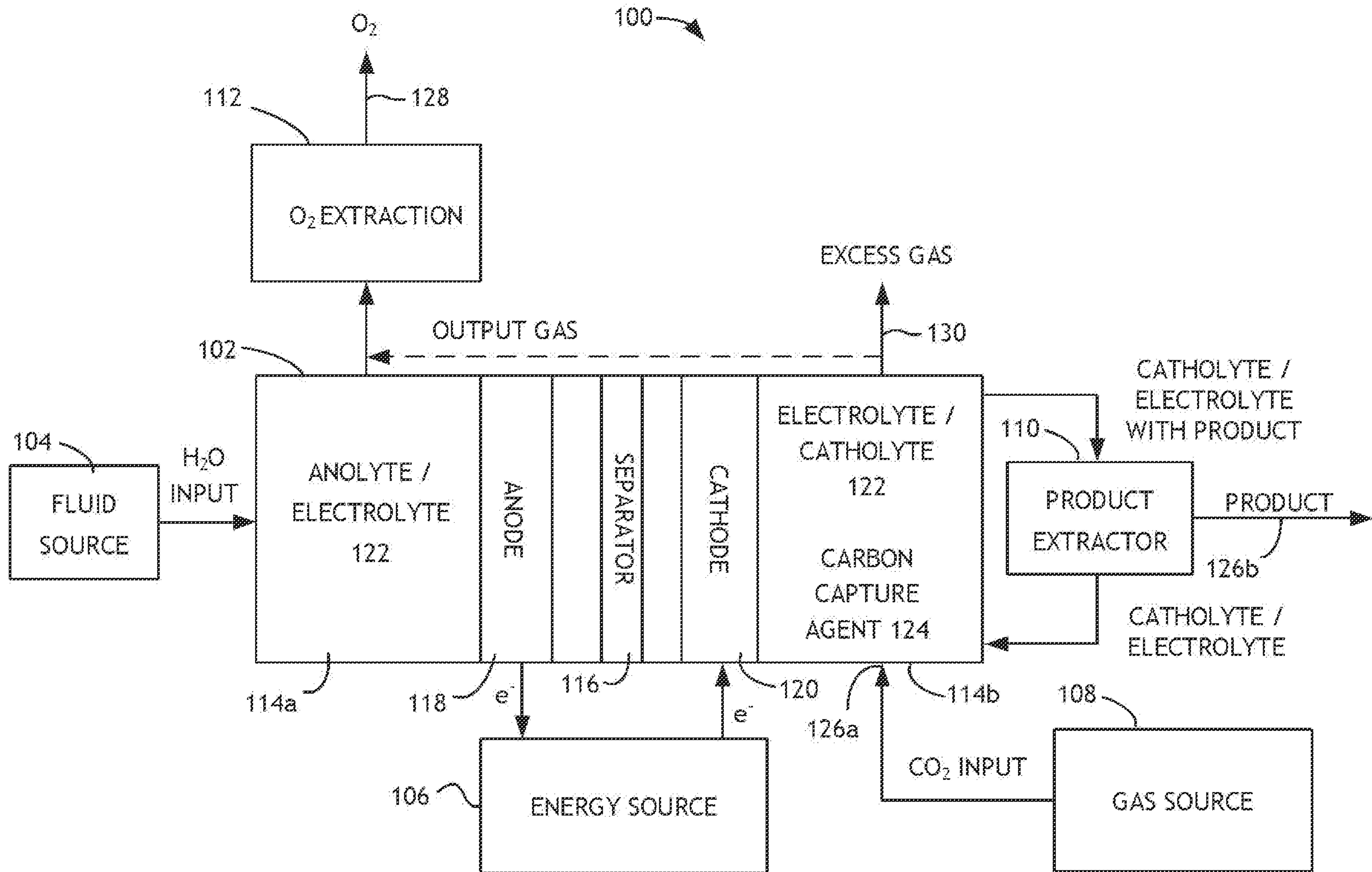


FIG. 1A