



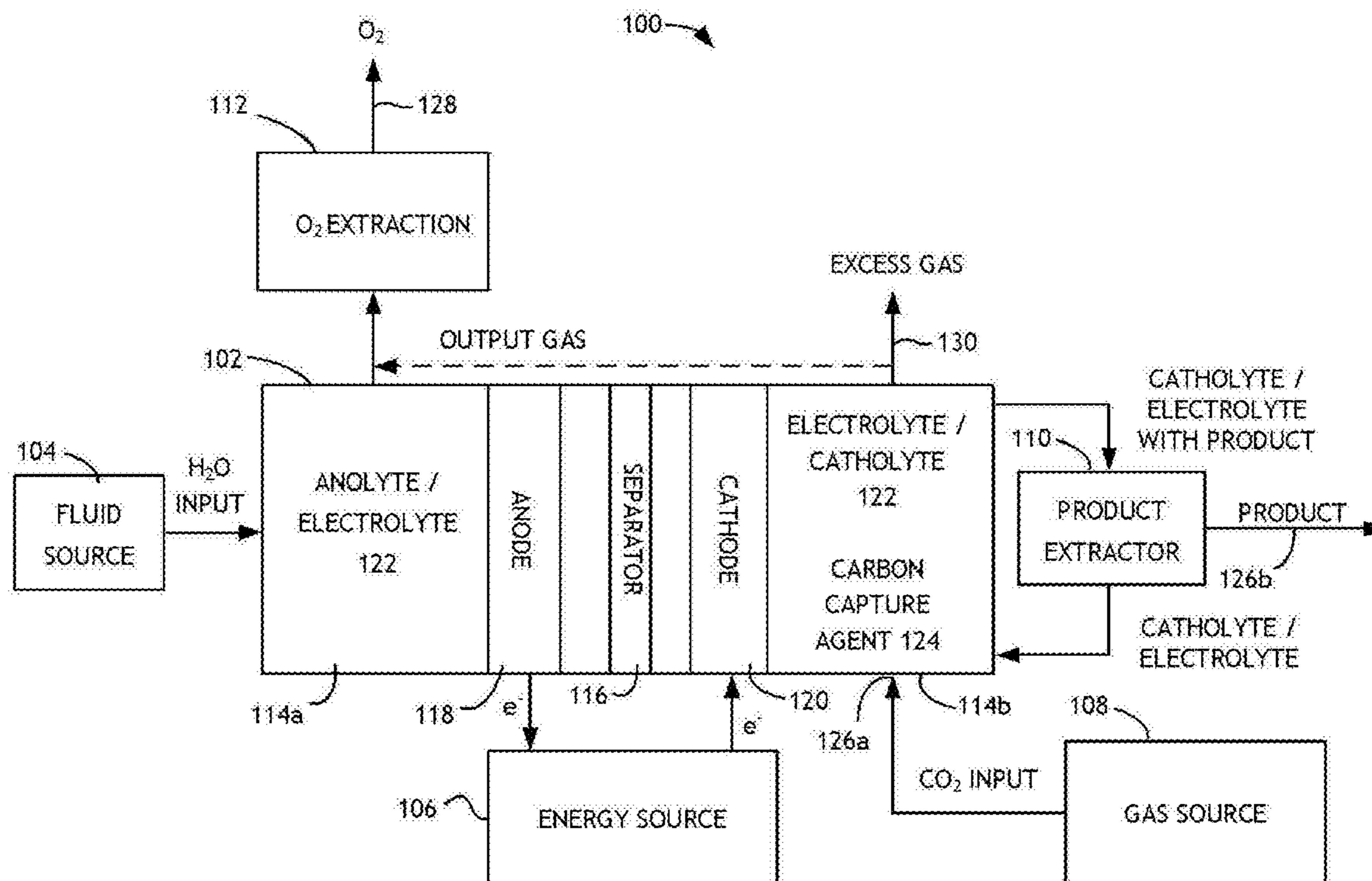
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Lakkaraju et al.(10) **Pub. No.: US 2014/0183038 A1**(43) **Pub. Date: Jul. 3, 2014**(54) **CARBON DIOXIDE CAPTURE AND
CONVERSION TO ORGANIC PRODUCTS****Publication Classification**(71) Applicant: **Liquid Light, Inc.**, Monmouth Junction,
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2012, now Pat. No. 8,658,016.(60) Provisional application No. 61/504,828, filed on Jul. 6,
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(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.



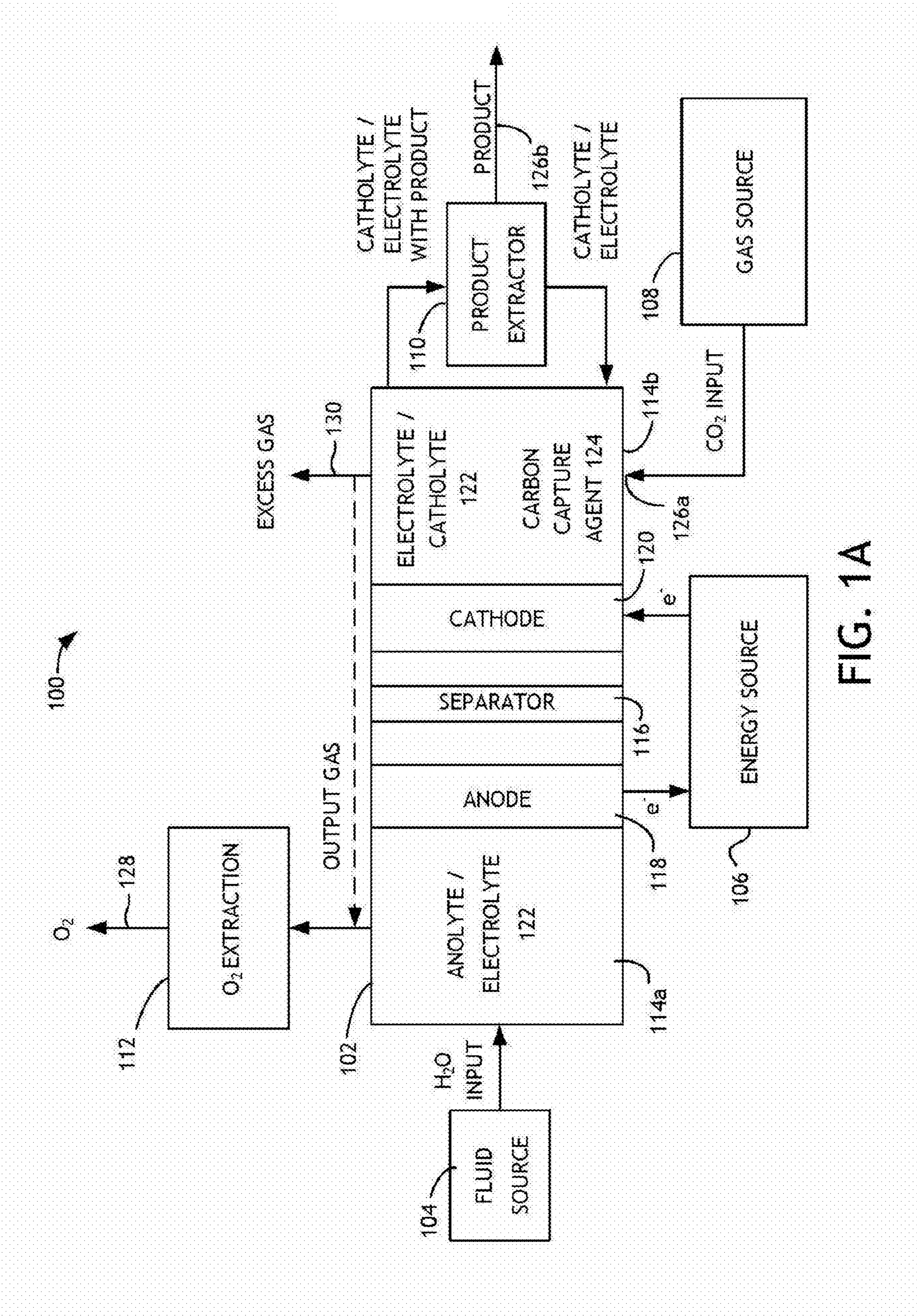


FIG. 1A

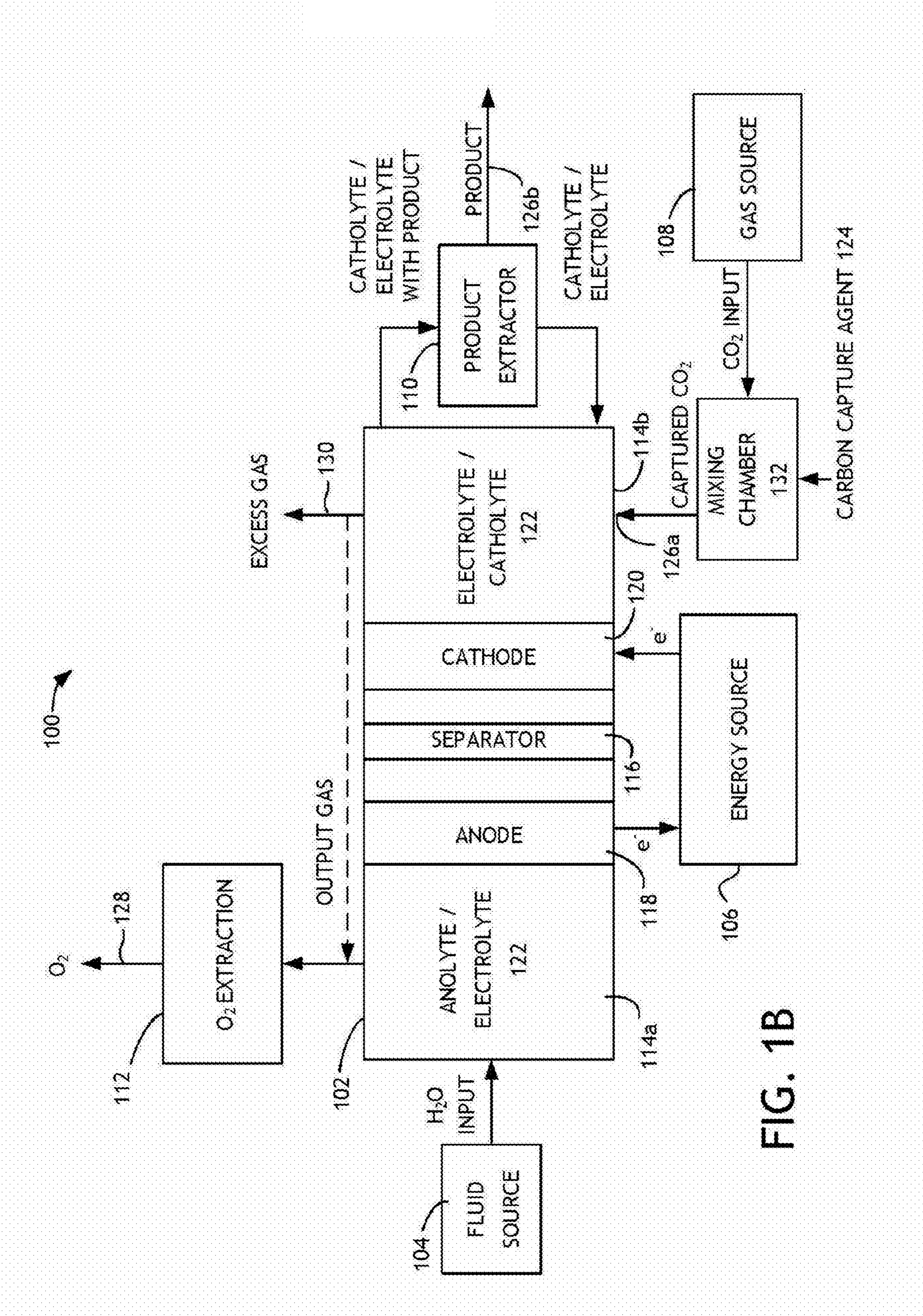


FIG. 1B

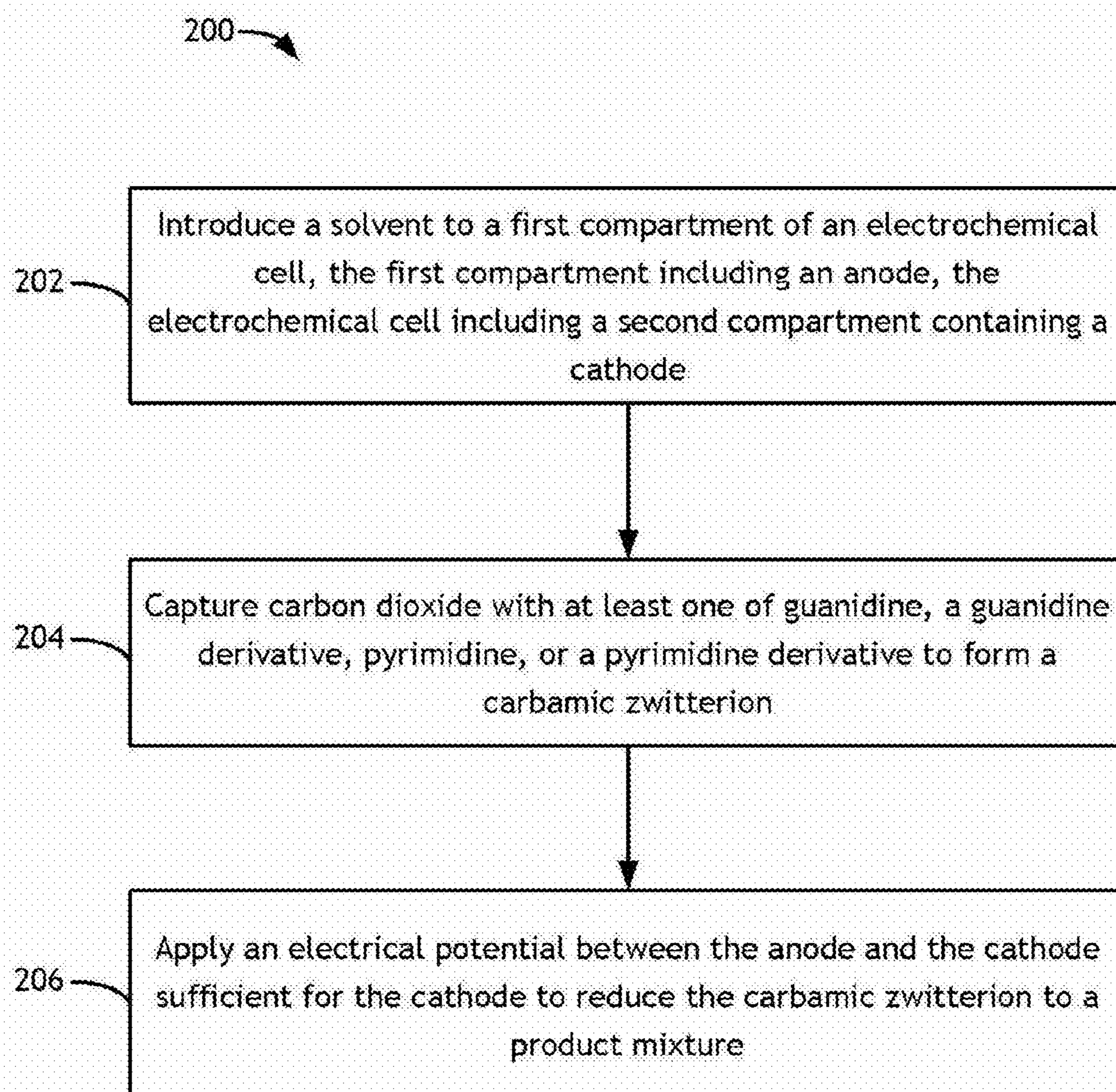


FIG. 2

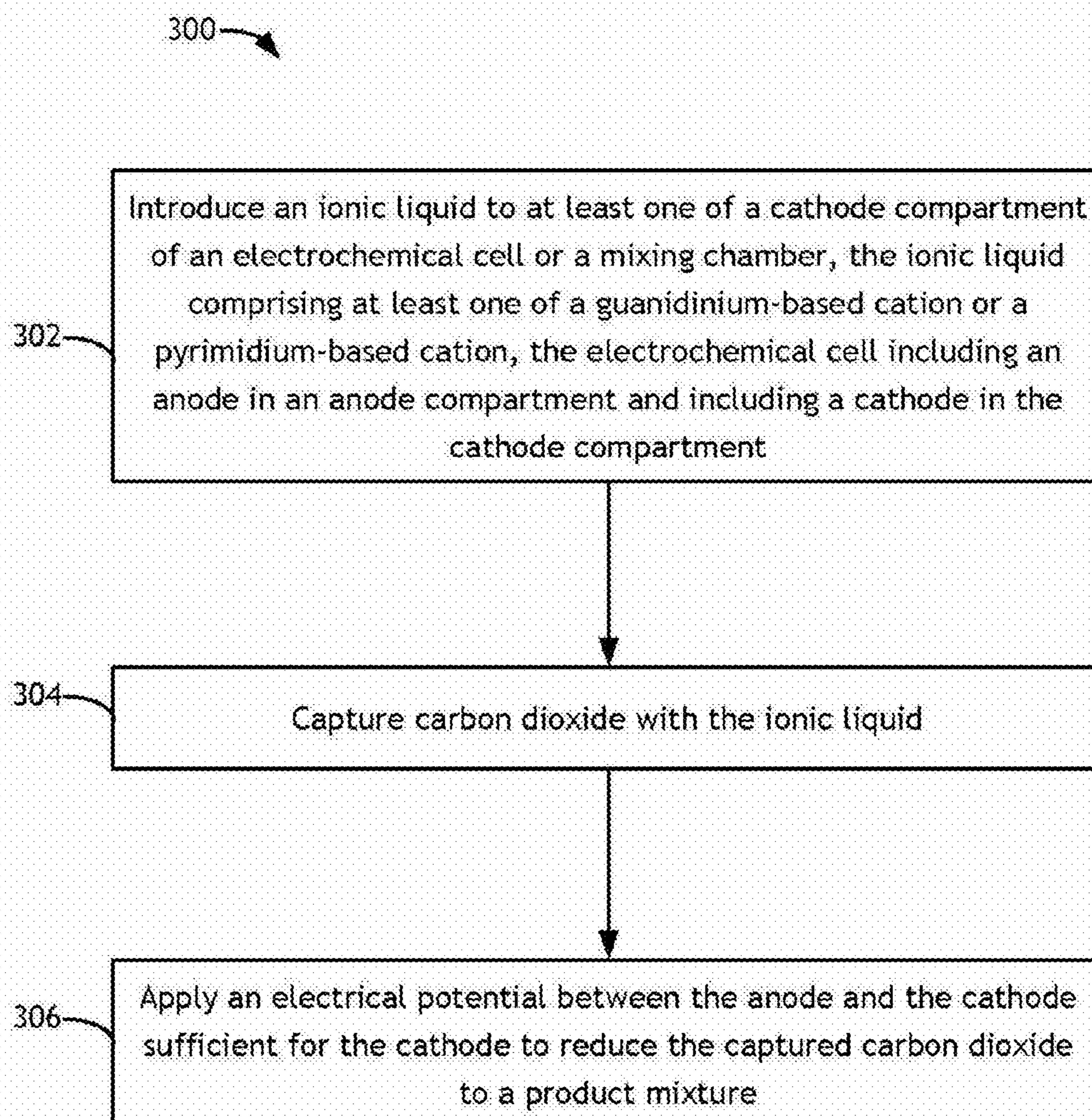


FIG. 3

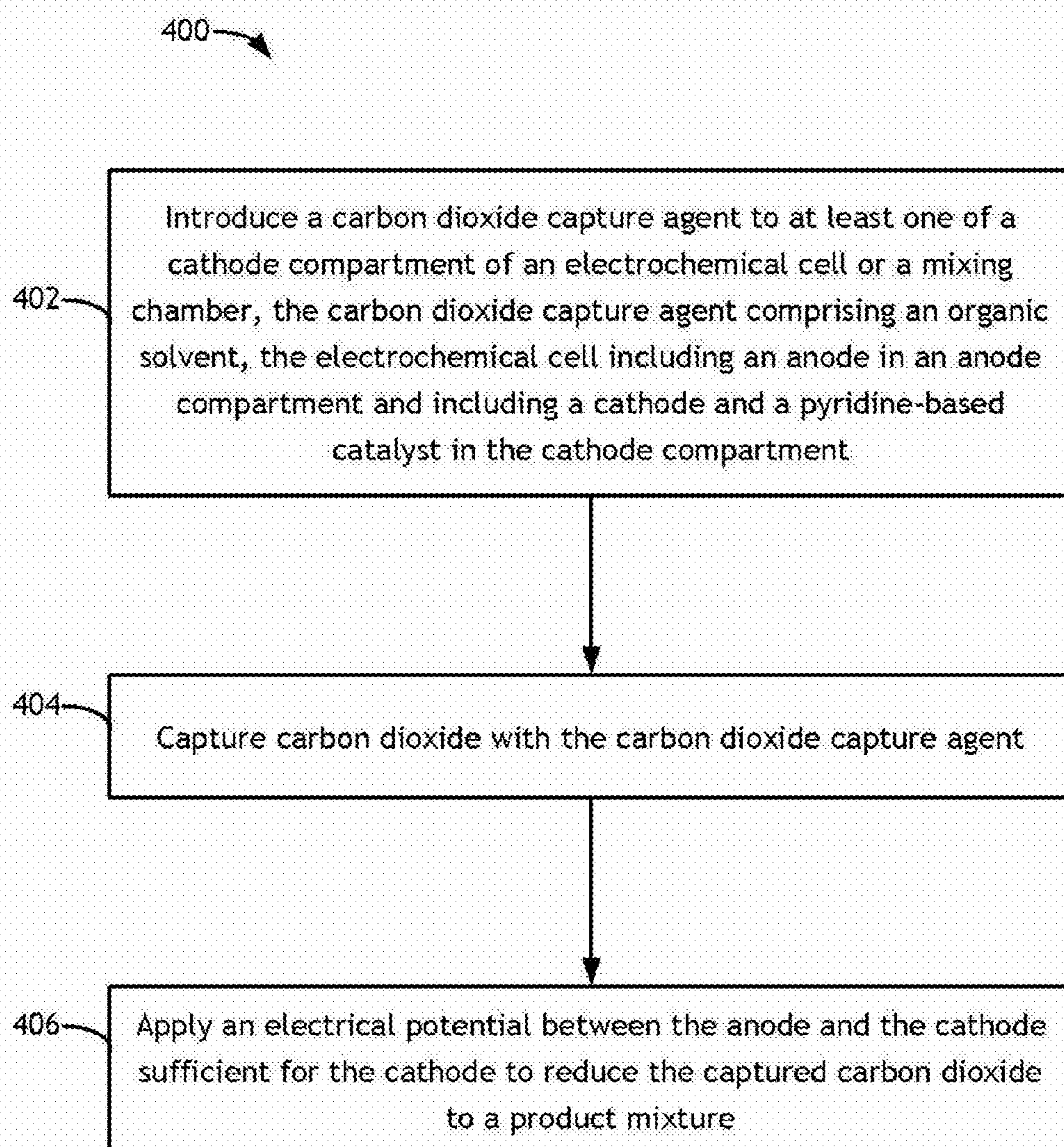


FIG. 4

CARBON DIOXIDE CAPTURE AND CONVERSION TO ORGANIC PRODUCTS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit under 35 U.S.C. §120 of U.S. application Ser. No. 13/541,933 filed Jul. 5, 2012. The U.S. application Ser. No. 13/541,933 filed Jul. 5, 2012 claims the benefit under 35 U.S.C. §119(e) of U.S. Patent Application Ser. No. 61/504,828, filed Jul. 6, 2011.

[0002] The above-listed applications are hereby incorporated by reference in its entirety.

FIELD

[0003] The present disclosure generally relates to the field of 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

[0004] 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 potentially damaging effects. Countries around the world, including the United States, are seeking ways to mitigate emissions of carbon dioxide.

[0005] A mechanism for mitigating emissions is to convert carbon dioxide into economically valuable materials such as fuels and industrial 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

[0006] 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 thereof.

[0007] 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

[0008] 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:

[0009] FIG. 1A is a block diagram of a preferred system in accordance with an embodiment of the present disclosure;

[0010] FIG. 1B is a block diagram of a preferred system in accordance with another embodiment of the present disclosure;

[0011] FIG. 2 is a flow diagram of a preferred method of capture of carbon dioxide and electrochemical conversion of the carbon dioxide;

[0012] FIG. 3 is a flow diagram of another preferred method of capture of carbon dioxide and electrochemical conversion of the carbon dioxide; and

[0013] 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

[0014] 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.

[0015] 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.

[0016] 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.

[0017] 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.

[0018] 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.

[0019] 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.

[0020] 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 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 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 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 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**.

[0021] In a particular implementation, the carbon dioxide capture agent **124** includes at least one of guanidine or a guanidine derivative. Carbon dioxide capture agent **124** may 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.

[0022] 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.

[0023] 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.

[0024] 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.

[0025] The fluid source **104** preferably includes a water source, such that 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 agent **124** is an ionic liquid, the fluid source **104** may provide the ionic liquid to the cell **102**.

[0026] The energy source **106** may include a variable electrical power source. The energy source **106** may be operational to generate an 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.

[0027] 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 **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 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 **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**.

[0028] Advantageously, the carbon dioxide may be obtained from any 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 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 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 allow the carbon dioxide to be a renewable and essentially unlimited source of carbon.

[0029] The product extractor **110** may include an organic product and/or inorganic product extractor. The product extractor **110** generally 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 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 compartment **114b** for capture of additional carbon dioxide.

[0030] The oxygen extractor **112** of FIG. 1 is generally operational to extract oxygen (e.g., O_2) byproducts created by the reduction of the carbon dioxide and/or the oxidation of water. In preferred 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 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**.

[0031] 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 method **200** may be implemented using the system **100**.

[0032] 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.

[0033] 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**.

[0034] 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.

[0035] 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**.

[0036] 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.

[0037] 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.

What is claimed is:

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

an electrochemical cell including:

a first cell compartment;

an anode positioned within said first cell compartment;

a second cell compartment;

a cathode positioned within said second cell compartment, the second cell compartment including a carbamic zwitterion; and

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.

2. The system of claim **1**, wherein the carbamic zwitterion is formed in the second cell compartment by interacting carbon dioxide with at least one of guanidine or a guanidine derivative.

3. The system of claim **1**, wherein the carbamic zwitterion is formed in a mixing chamber by interacting carbon dioxide with at least one of guanidine or a guanidine derivative prior to introduction to said second cell compartment.

4. The system of claim **1**, wherein the energy source is further configured to apply a voltage between said anode and said cathode to regenerate a guanidine or a guanidine derivative.

5. The system 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.

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