



US 20140034506A1

(19) **United States**

(12) **Patent Application Publication**
Teamey et al.

(10) **Pub. No.: US 2014/0034506 A1**

(43) **Pub. Date: Feb. 6, 2014**

(54) **SYSTEM AND METHOD FOR OXIDIZING ORGANIC COMPOUNDS WHILE REDUCING CARBON DIOXIDE**

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(21) Appl. No.: **14/036,571**

(22) Filed: **Sep. 25, 2013**

Related U.S. Application Data

(62) Division of application No. 13/724,082, filed on Dec. 21, 2012.

(60) Provisional application No. 61/720,670, filed on Oct. 31, 2012, provisional application No. 61/703,238, filed on Sep. 19, 2012, provisional application No. 61/675,938, filed on Jul. 26, 2012, provisional application No. 61/703,229, filed on Sep. 19, 2012, provisional application No. 61/703,175, filed on Sep. 19,

2012, provisional application No. 61/703,231, filed on Sep. 19, 2012, provisional application No. 61/703,232, filed on Sep. 19, 2012, provisional application No. 61/703,234, filed on Sep. 19, 2012, provisional application No. 61/703,158, filed on Sep. 19, 2012, provisional application No. 61/703,187, filed on Sep. 19, 2012.

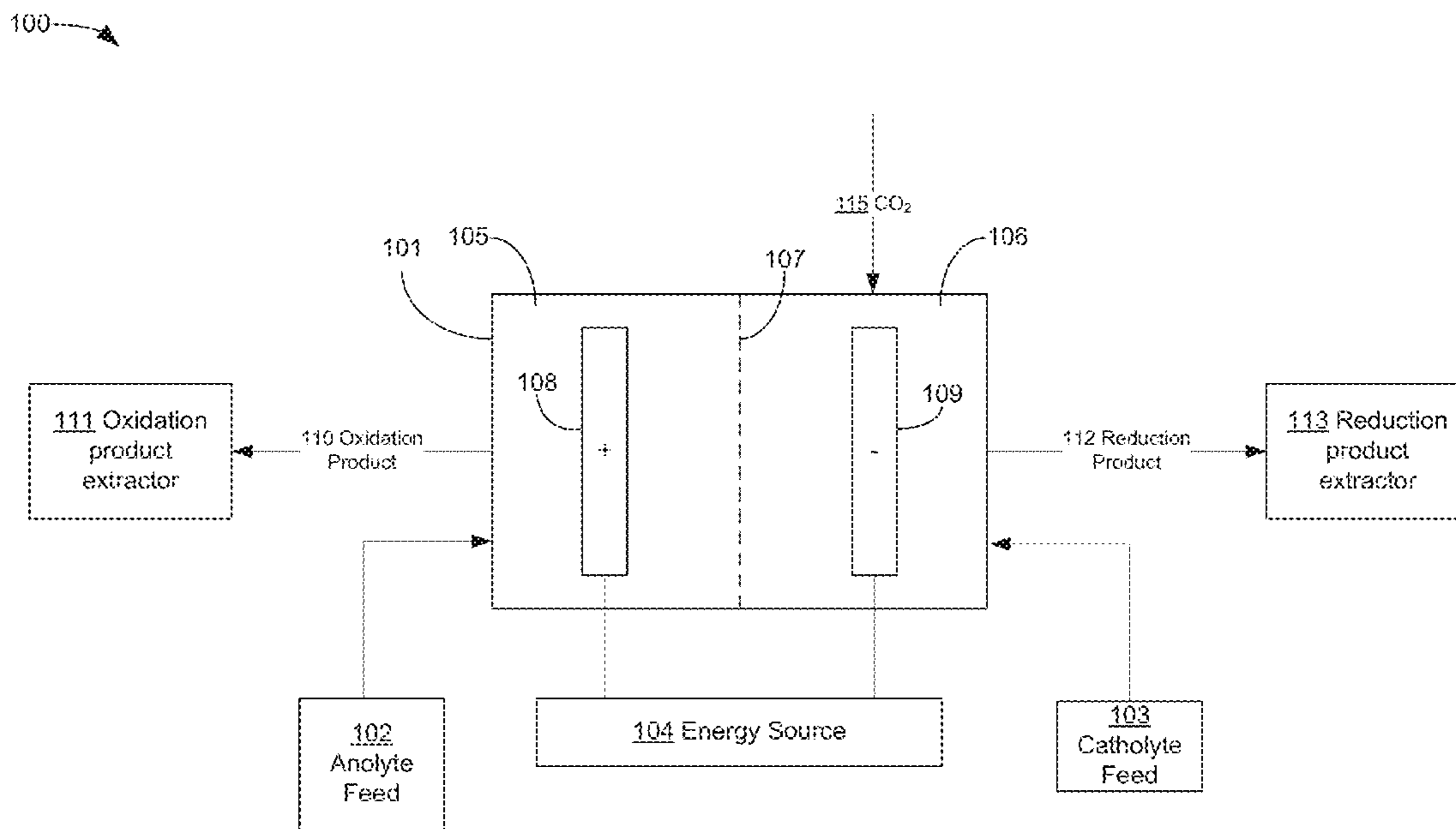
Publication Classification

(51) **Int. Cl.**
C25B 3/02 (2006.01)
C25B 3/04 (2006.01)
C25B 9/08 (2006.01)

(52) **U.S. Cl.**
CPC ... **C25B 3/02** (2013.01); **C25B 9/08** (2013.01); **C25B 3/04** (2013.01)
USPC **205/349**; 204/263; 205/334; 205/440; 205/439; 205/436; 205/413; 205/551; 205/464; 205/452; 205/447; 205/449; 205/637; 205/555; 205/448; 205/450; 205/462; 205/455; 205/427

(57) **ABSTRACT**

Methods and systems for electrochemically generating an oxidation product and a reduction product may include one or more operations including, but not limited to: receiving a feed of at least one organic compound into an anolyte region of an electrochemical cell including an anode; at least partially oxidizing the at least one organic compound at the anode to generate at least carbon dioxide; receiving a feed including carbon dioxide into a catholyte region of the electrochemical cell including a cathode; and at least partially reducing carbon dioxide to generate a reduction product at the cathode.



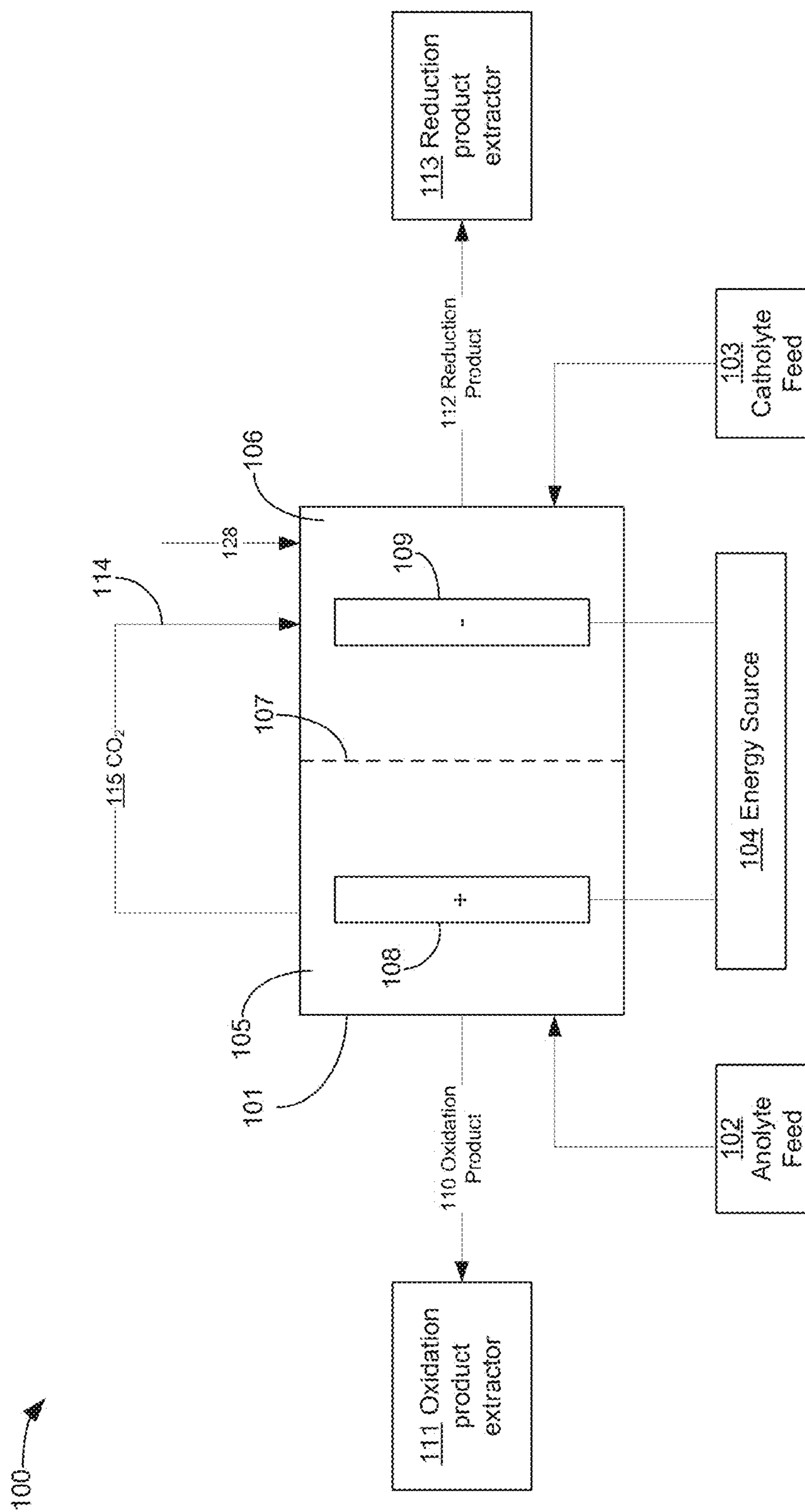


FIG. 1

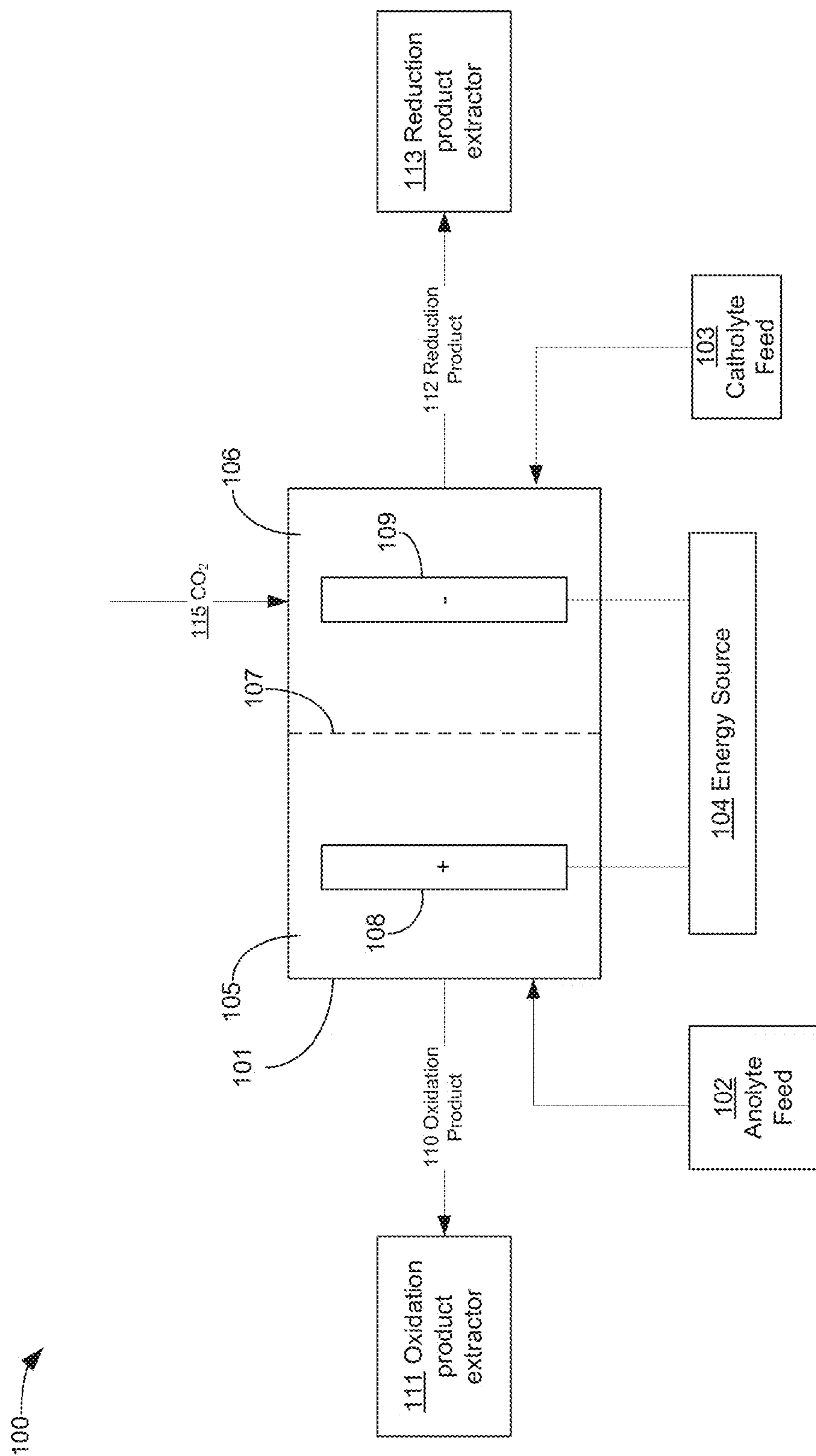


FIG. 2

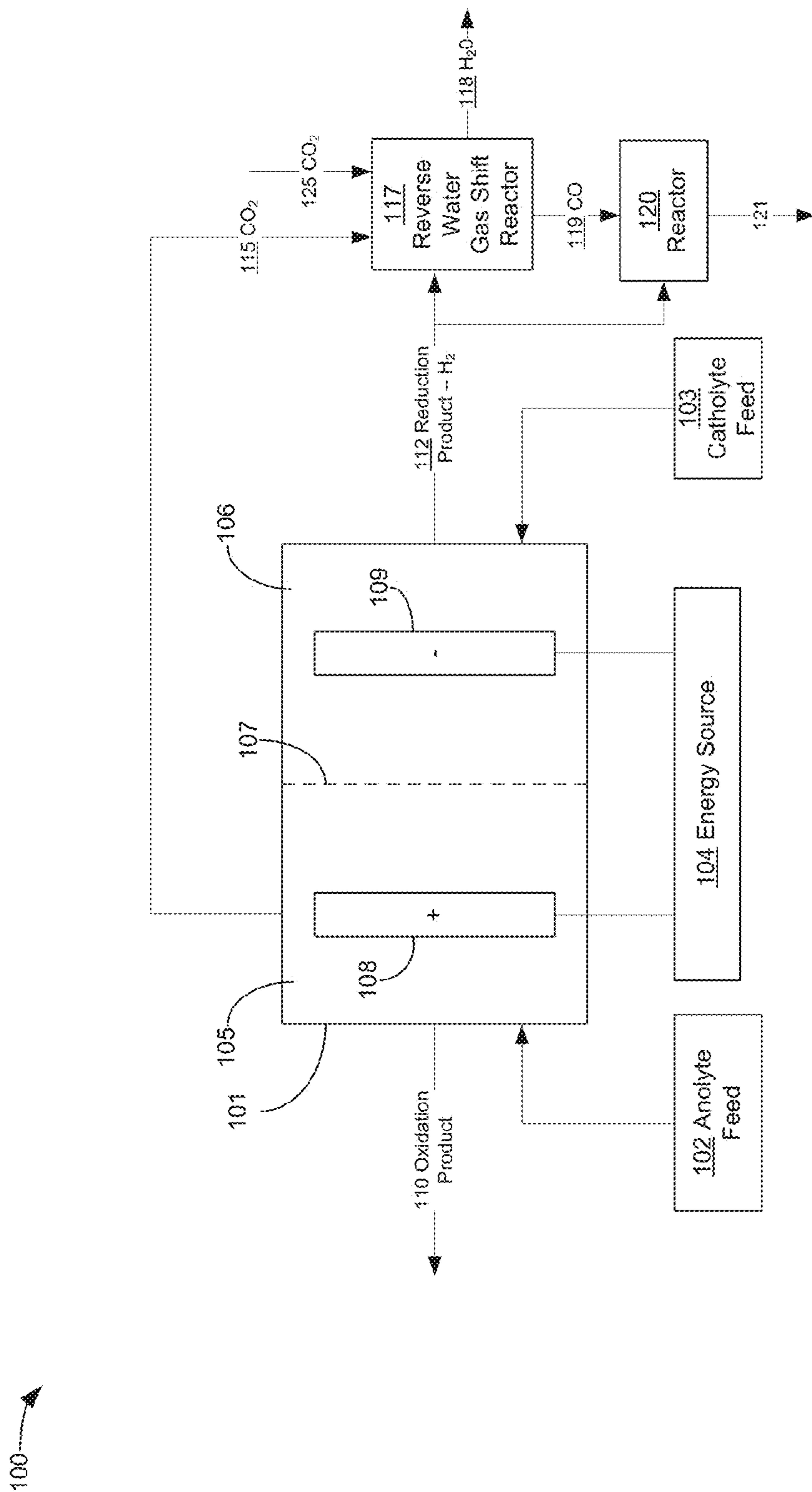


FIG. 3

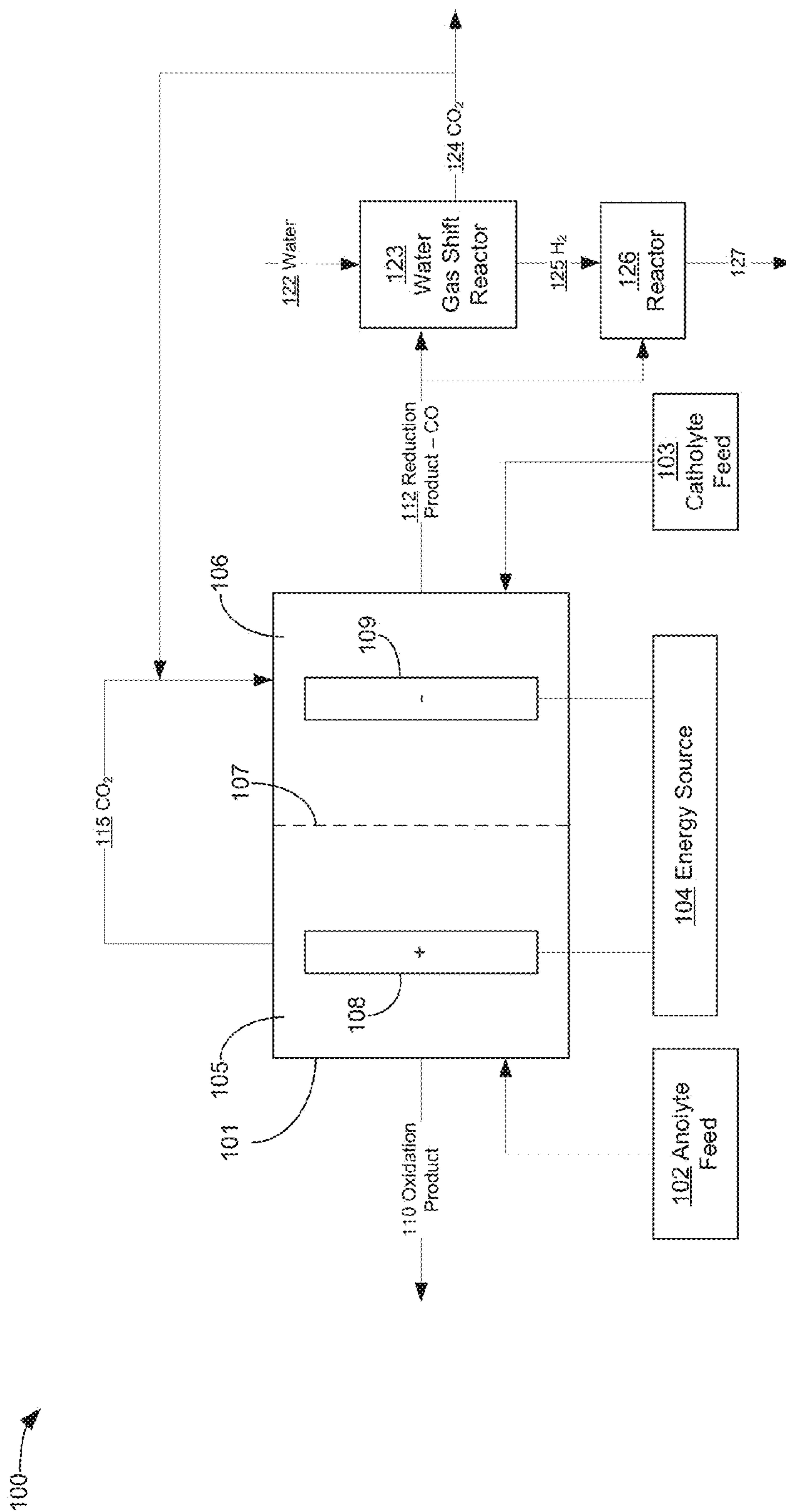


FIG. 4

**SYSTEM AND METHOD FOR OXIDIZING
ORGANIC COMPOUNDS WHILE REDUCING
CARBON DIOXIDE**

CROSS-REFERENCE TO RELATED
APPLICATIONS

[0001] The present application claims the benefit under 35 U.S.C. §119(e) of U.S. Provisional Application Ser. No. 61/720,670 filed Oct. 31, 2012, U.S. Provisional Application Ser. No. 61/703,238 filed Sep. 19, 2012 and U.S. Provisional Application Ser. No. 61/675,938 filed Jul. 26, 2012. Said U.S. Provisional Application Ser. No. 61/720,670 filed Oct. 31, 2012, U.S. Provisional Application Ser. No. 61/703,238 filed Sep. 19, 2012 and U.S. Provisional Application Ser. No. 61/675,938 filed Jul. 26, 2012 are incorporated by reference in their entireties.

[0002] The present application also claims the benefit under 35 U.S.C. §119(e) of U.S. Provisional Application Ser. No. 61/703,229 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,175 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,231 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,232, filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,234, filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,158 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,187 filed Sep. 19, 2012. The U.S. Provisional Application Ser. No. 61/703,229 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,175 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,231 filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,232, filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,234, filed Sep. 19, 2012, U.S. Provisional Application Ser. No. 61/703,158 filed Sep. 19, 2012 and U.S. Provisional Application Ser. No. 61/703,187 filed Sep. 19, 2012 are hereby incorporated by reference in their entireties.

[0003] The present application incorporates by reference co-pending U.S. patent application Attorney Docket 0022, U.S. patent application Attorney Docket 0023, U.S. patent application Attorney Docket 0024 U.S. patent application Attorney Docket 0025, U.S. patent application Attorney Docket 0026, U.S. patent application Attorney Docket 0027, U.S. patent application Attorney Docket 0028, and U.S. patent application Attorney Docket 0030 in their entireties.

TECHNICAL FIELD

[0004] The present disclosure generally relates to the field of electrochemical reactions, and more particularly to methods and/or systems for oxidizing organic compounds while reducing carbon dioxide.

BACKGROUND

[0005] 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.

[0006] 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 con-

verted 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 will be possible.

SUMMARY OF THE PREFERRED
EMBODIMENTS

[0007] Methods and systems for electrochemically generating an oxidation product and a reduction product may include one or more operations including, but not limited to: receiving a feed of at least one organic compound into an anolyte region of an electrochemical cell including an anode; at least partially oxidizing the at least one organic compound at the anode to generate at least carbon dioxide; receiving a feed including carbon dioxide into a catholyte region of the electrochemical cell including a cathode; and at least partially reducing carbon dioxide to generate a reduction product at the cathode.

[0008] 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 present disclosure. The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate subject matter of the disclosure. Together, the descriptions and the drawings serve to explain the principles of the disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The numerous advantages of the disclosure may be better understood by those skilled in the art by reference to the accompanying figures in which:

[0010] FIGS. 1-4 illustrate systems for electrochemically generating an oxidation product and a reduction product.

DETAILED DESCRIPTION

[0011] Reference will now be made in detail to the subject matter disclosed, which is illustrated in the accompanying drawings.

[0012] Referring generally to FIGS. 1-4, systems and methods of electrochemical co-production of products with a carbon-based reactant feed to an anode are disclosed. It is contemplated that the electrochemical co-production of products may include production of an oxidation product, such as an oxidized carbon-based product from an organic compound feed at the anode side of an electrochemical cell with co-production of a reduction product, such as reduction of carbon dioxide generated in the oxidation reaction to carbon-based products to include one, two, three, and four carbon chemicals at a cathode side of the electrochemical cell.

[0013] Before any embodiments of the disclosure are explained in detail, it is to be understood that the embodiments may not be limited in application per the details of the structure or the function as set forth in the following descriptions or illustrated in the figures. Different embodiments may be capable of being practiced or carried out in various ways. 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. It is further contemplated that like reference numbers may describe similar components and the equivalents thereof.

[0014] The present invention encompasses oxidation or partial oxidation of an organic or carbon-containing compound at the anode of the electrochemical cell and an at least partially simultaneous reduction of carbon dioxide generated in the oxidation reaction to carbon-based products to include one, two, three, and four carbon chemicals at the cathode side of an electrochemical cell. If the anode is utilized for waste remediation, the organic compound may be oxidized to carbon dioxide and low toxicity products or partially oxidized to a compound which can be further oxidized by bacteria to carbon dioxide and water. The carbon dioxide may then be recycled into the cathode side of the electrochemical cell. If the anode is utilized for production of organic products, an organic compound may be partially oxidized to another valuable compound.

[0015] Referring to FIG. 1, a block diagram of a system **100** in accordance with an embodiment of the present disclosure is shown. The system **100** (or apparatus) generally includes an electrochemical cell **101** (also referred as a container, electrolyzer, or cell), an anolyte feed **102** including an organic compound, a catholyte feed **103** and an energy source **104**.

[0016] The electrochemical cell **101** may be implemented as a divided cell. The divided cell may be a divided electrochemical cell and/or a divided photoelectrochemical cell. The electrochemical cell **101** may include an anolyte region **105** and a catholyte region **106** divided by separator **107**. The anolyte region **105** may include an anode **108**. The catholyte region **106** may include a cathode **109**. The anolyte region **105** may include an anolyte which may include an anolyte feed **102** including an organic compound. The catholyte region **106** may include a catholyte feed **103** whereby carbon dioxide is dissolved in the catholyte. The energy source **104** may generate an electrical potential between the anode **108** and the cathode **109**. The electrical potential may be a DC voltage. The energy source **104** may be configured to implement a variable voltage or constant current source.

[0017] In an embodiment of the invention the electrochemical cell **101** may produce valuable chemicals at the cathode **109** and remove or oxidize organic compounds from the anolyte feed **102** at the anode **108**. The cathode **109** may be used to reduce carbon dioxide to carbon-containing chemicals. By using this process, the overall energy requirement for making the chemical at the cathode **109** and removing or oxidizing a contaminant at the anode **108** may be reduced by 50% or more. In addition, the oxidation product **110** generated from the organic compound may itself be a valuable product.

[0018] The electrochemical cell **101** may be operational to electrochemically produce an oxidation product **110** recoverable from the anolyte region **105** by an oxidation product extractor **111** while electrochemically reducing carbon dioxide in the catholyte region **106** to a reduction product **112** (e.g. a C₁ to C₄ reduction product) recoverable from the catholyte region **106** by a reduction product extractor **113**.

[0019] The anode **108** reaction occurring in the anolyte region **105** may include a variety of partial and full oxidations of an organic contaminant in the anolyte feed **102** to the oxidation product **110**. Oxidations may be direct, such as the conversion of ethane to ethanol at the anode. They also may

be indirect, such as conversion of ethane to ethanol utilizing a halogenated compound produced at the anode. Examples are in Table 1 below:

TABLE 1

Organic Compound in Anolyte Feed 102	Oxidation Product(s)
A carboxylic acid such as formic acid	CO ₂
An aldehyde or ketone such as formaldehyde	A carboxylic acid such as formic acid or CO ₂
Alcohol such as ethanol	Acetic Acid, oxalic acid, CO ₂
A glycol such as ethylene glycol	Organic acids or CO ₂
An alkane such as dodecane	Organic acids or CO ₂
An unsaturated alkene organic chemical such as linoleic acid	Organic acids or CO ₂
An aromatic compound such as benzene or phenol	Organic acids or CO ₂
Cyanide	Cyanate, carbonate, CO ₂ , and nitrogen compounds
Surfactants such as lauryl sulfate	Organic acids, CO ₂ , or salts
A halogenated carbon compound such as chlorophenol	Dehalogenated organics, dehalogenated organic acids, or halide salts
Methane	Methanol, formaldehyde, formic acid
Ethane	Ethanol, Acetaldehyde, Acetic Acid
Ethylene	Ethylene oxide
Propane	Propylene, Propanol, propanoic acid, or other C3 chemicals
Propene	Propylene oxide, allyl alcohol
Butane	Butene, butadiene, butanol, or other C4 chemicals
Butene	Butadiene
Isobutane	Isobutylene, isobutyl alcohols
Ethylbenzene	Styrene
Ethyl acetate	Vinyl acetate
Methyl propionate, Ethyl propionate	Methyl acrylate, ethyl acrylate
Propionitrile	Acrylonitrile
Benzene	Phenol
Phenol	Hydroquinone, 1-2 dihydrobenzene (Catechol), 2,5 Cyclohexadiene-1-one, Benzoquinone, Maleic Acid, Oxalic Acid

[0020] In an embodiment of the invention, CO₂ **115** and/or an oxidation product **110** may be produced during an oxidation reaction at the anode **108**. The CO₂ **115** may be provided to the catholyte region **106** via a gas/fluid coupling **114**. Additionally, a supplemental feed **128** including at least CO₂ may be provided to the catholyte region **106**. The cathode **109** reaction occurring in the catholyte region **106** may then reduce the CO₂ **115** produced during the anode **108** reaction occurring in the anolyte region **105** and/or the supplemental feed **128** including at least CO₂ with the catholyte feed **103** to produce a reduction product **112** that may include one or more compounds. Examples of the reduction product **112** recoverable from the catholyte region **106** by reduction product extractor **113** may include carbon monoxide, formic acid, formaldehyde, methanol, oxalate, oxalic acid, glyoxylic acid, glycolic acid, glyoxal, glycolaldehyde, ethylene glycol, acetic acid, acetaldehyde, ethanol, lactic acid, propanoic acid, acetone, isopropanol, 1-propanol, 1,2-propylene glycol, 1-butanol, and/or 2-butanol.

[0021] In a specific embodiment, the oxidation reaction at the anode **108** may generate CO₂ **115** and an oxidation product **110** including acetic acid produced from oxidation of an anolyte feed **102** including waste phenol in the presence of water. The reduction product **112** may be acetic acid gener-

ated from a direct reduction of the co-generated CO₂ **115** at the cathode **109**. The reaction at the anode **108** is $C_6H_5OH + 11H_2O \Rightarrow 6CO_2 + 28H^+ + 28e^-$. The reaction at the cathode **109** is $7CO_2 + 28H^+ + 28e^- \Rightarrow 3\frac{1}{2} CH_3COOH + 7H_2O$. The overall reaction for the electrochemical cell **101** is $C_6H_5OH + 4H_2O \Rightarrow 3\frac{1}{2} CH_3COOH$.

[0022] In other embodiments, the anode **108** may include electrocatalytic materials that have high oxygen overpotentials and thus help to preferentially oxidize organic compounds rather than water. Example materials include lead dioxide, tin oxides, electrically conductive titanium sub-oxides such as Ebonex (Ti₄O₇) with or without additional high oxidation overpotential electrocatalyst coatings, as well as boron doped diamond films on metal or electrically conductive substrates. If a partial oxidation is desired, this may be accomplished with a wide variety of precious metals and their oxides such as platinum, palladium, gold, ruthenium and iridium that are deposited on valve metal substrates such as titanium, niobium, and tantalum, in addition to transition metals and their oxides, other non-transition metal oxides, and stainless steels so long as the anode potential is less than that required for the oxidation of water and the anode material and/or coating electrocatalyst is stable in the particular organic anode oxidation reaction.

[0023] Referring to FIG. 2, in another embodiment, an anolyte feed **102** including an alkane or alcohol may be directly oxidized at the anode **108** to generate an oxidation product **110**. Protons and electrons for reduction of CO₂ **115** may be provided to the cathode **109** while the oxidation product **110** is co-produced at the anode **108**. The anolyte feed **102** including the alkane or alkene may be directly oxidized to an oxidation product **110** such as an alcohol or organic acid or oxide. In a specific embodiment, the anolyte feed **102** may include ethane which may be oxidized to an oxidation product **110** including ethanol. On the cathode **109** side, CO₂ **115** may be reacted on a high surface area cathode **109** to produce, for example, sodium acetate and byproduct hydrogen. A circulation pump may be used to provide mass transfer to obtain a high current Faradaic efficiency conversion to a reduction product **112** including acetate. The reduction product **112** may overflow the catholyte loop, and may later be converted (e.g. by the reduction product extractor **113**) to an acetic acid form using an electrochemical acidification unit and concentrated by evaporation and/or distillation method. The overall reaction for the electrochemical cell **101** is $2CO_2 + 4O_2H_6 + 2H_2O \Rightarrow CH_3COOH + 4C_2H_5OH$.

[0024] The reaction occurring at the anode **108** may occur in gas phase, for instance in the case of gas phase reactants such as methane. The anode **108** reaction may also occur in liquid phase, such as the case of an organic in solution. Preferably, the reaction at the anode **108** occurs in the gas phase and the anolyte region **105** includes water vapor. Reactions occurring at the cathode **109** may take place in a solvent selected from water, methanol, acetonitrile, propylene carbonate, ionic liquids, and/or other solvents in which CO₂ **115** is soluble.

[0025] The electrochemical cell **101** may be: 1) liquid phase at both the anode **108** in the anolyte region **105** and the cathode **109** in the catholyte region **106**; 2) gas phase at the anode **108** in the anolyte region **105** where gas phase ethane and water vapor may be fed directly to the anode **108** and liquid phase at the cathode **109** in the catholyte region **106**.

[0026] The electrochemical cell **101** may be operated at a current density of greater than 3 kA/m² (300 mA/cm²), or in

suitable range of 0.5 to 5 kA/m² or higher. The operating voltage of the system at a current density of 1 kA/m² may be between 1.0-3.5 volts.

[0027] The anode **108**, for example, may be a polymeric bound carbon current distributor anode including a carbon felt that is mechanically or chemically bonded to the current distributor with a specific surface area of at least 50 cm²/cm³ that is electrically connected to the current distributor and may fill a gap between a current distributor backplate of the cathode **109** and the separator **107**, thus having a zero-gap anode **108**. Precious and transition metals and/or precious and transition metal oxide catalysts (e.g. a RuO₂ catalyst) may be added or incorporated into the structure of anode **108** in order to decrease anode potential and/or increase anode current density.

[0028] The cathode **109** may include high surface area materials such as copper, stainless steels, carbon, and silicon, which may be further coated with a layer of material which may be a conductive metal or semiconductor. There may be a very thin plastic screen against the cathode-side of the separator **107** to prevent the separator **107** from touching the high surface area cathode **109**. The high surface area cathode **109** may be mechanically pressed against or bonded to a cathode current distributor backplate, which may be composed of material that has the same surface composition as the high surface area cathode. Preferred void volume for the cathode **109** may range from 30% to 98%. The surface area of the high surface area cathode **109** may be from 2 cm²/cm³ to 500 cm²/cm³ or higher. The surface area may also be defined as total area in comparison to a current distributor/conductor back plate, with a preferred range of 2× to 1000× or more. The actual total active surface area of the electrode structure is a function of the properties of the electrode catalyst deposited on the physical electrode structure which may be 2 to 1000 times higher in surface area than the physical electrode base structure.

[0029] For electrochemical reductions, the cathode electrode may be a suitable conductive electrode, such as Al, Au, Ag, Bi, C, Cd, Co, Cr, Cu, Cu alloys (e.g., brass and bronze), Ga, Hg, In, Mo, Nb, Ni, NiCo₂O₄, Ni alloys (e.g., Ni 625, NiHX), Ni—Fe alloys, Pb, Pd alloys (e.g., PdAg), Pt, Pt alloys (e.g., PtRh), Rh, Sn, Sn alloys (e.g., SnAg, SnPb, SnSb), Ti, V, W, Zn, stainless steel (SS) (e.g., SS 2205, SS 304, SS 316, SS 321), austenitic steel, ferritic steel, duplex steel, martensitic steel, Nichrome (e.g., NiCr 60:16 (with Fe)), elgiloy (e.g., Co—Ni—Cr), degenerately doped p-Si, degenerately doped p-Si:As, degenerately doped p-Si:B, degenerately doped n-Si, degenerately doped n-Si:As, and degenerately doped n-Si:B. Other conductive electrodes may be implemented to meet the criteria of a particular application. For photoelectrochemical reductions, the electrode may be a p-type semiconductor, such as p-GaAs, p-GaP, p-InN, p-InP, p-CdTe, p-GaInP₂ and p-Si, or an n-type semiconductor, such as n-GaAs, n-GaP, n-InN, n-InP, n-CdTe, n-GaInP₂ and n-Si. Other semiconductor electrodes may be implemented to meet the criteria of a particular application including, but not limited to, CoS, MoS₂, TiB, WS₂, SnS, Ag₂S, CoP₂, Fe₃P, Mn₃P₂, MoP, Ni₂Si, MoSi₂, WSi₂, CoSi₂, Ti₄O₇, SnO₂, GaAs, GaSb, Ge, and CdSe.

[0030] Faradaic current efficiency of the anode **108** may be between 20 and 100%, and preferably greater than 25%, and the Faradaic current efficiency of the cathode **109** may be between 20 and 100% and preferably greater than 25%. The

flow circulation of the anolyte and catholyte may be such that it provides sufficient flow for the reactions.

[0031] Operating the electrochemical cell at higher pressures (e.g. above atmospheric) may increase the current efficiency and allow operation of the electrochemical cell **101** at higher current densities.

[0032] The anolyte feed **102** may have a pH in a range of 1 to 14 depending on the organic compound in the anolyte feed **102** to be oxidized and the anode **108** to be used for the oxidation to achieve an optimum oxidation conversion efficiency of the organic compound in the anolyte feed **102** to CO₂ **115**. The catholyte feed **103** may have a pH in a range from 3 to 12. The catholyte feed **103** pH may be a function of the catalysts used such that corrosion in the electrochemical cell **101** is limited. Such catalysts may include, but are not limited to, pyridine, 2-picoline, and other aromatic heterocyclic amines.

[0033] A catholyte feed **103** electrolyte may be selected from alkali metal bicarbonates, carbonates, sulfates, and phosphates, borates, and/or hydroxides. More specifically, bromide salts, such as NaBr or KBr may be used. The electrolyte may include one or more of Na₂SO₄, KCl, NaNO₃, NaCl, NaF, NaClO₄, KClO₄, K₂SiO₃, CaCl₂, a guanidinium cation, a H cation, an alkali metal cation, an ammonium cation, an alkylammonium cation, a tetraalkyl ammonium cation, a halide anion, an alkyl amine, a borate, a carbonate, a guanidinium derivative, a nitrite, a nitrate, a phosphate, a polyphosphate, a perchlorate, a silicate, a sulfate, and a hydroxide.

[0034] A catholyte or an anolyte may comprise an aqueous solvent, a non-aqueous solvent, or a mixture of solvents containing one or more of water as well as protic or aprotic polar solvents such as methanol, ethanol, acetonitrile, propylene carbonate, ethylene carbonate, dimethyl carbonate, diethyl carbonate, dimethylsulfoxide, dimethylformamide, acetonitrile, acetone, tetrahydrofuran, N,N-dimethylacetamide, dimethoxyethane, diethylene glycol dimethyl ester, butyrolonitrile, 1,2-difluorobenzene, γ -butyrolactone, N-methyl-2-pyrrolidone, sulfolane, 1,4-dioxane, nitrobenzene, nitromethane, acetic anhydride, and ionic liquids. An aqueous solvent comprises at least 5% water. A non-aqueous solvent comprises less than 5% water.

[0035] The catholyte may comprise a homogeneous catalyst. Homogeneous catalysts may comprise aromatic heterocyclic amines and may include, but are not limited to, unsubstituted and substituted pyridines and imidazoles. Substituted pyridines and imidazoles may include, but are not limited to mono and disubstituted pyridines and imidazoles. For example, suitable catalysts may include straight chain or branched chain lower alkyl (e.g., C1-C10) mono and disubstituted compounds such as 2-methylpyridine, 4-tertbutyl pyridine, 2,6 dimethylpyridine (2,6-lutidine); bipyridines, such as 4,4'-bipyridine; amino-substituted pyridines, such as 4-dimethylamino pyridine; and hydroxyl-substituted pyridines (e.g., 4-hydroxy-pyridine) and substituted or unsubstituted quinoline or isoquinolines. The catalysts may also suitably include substituted or unsubstituted dinitrogen heterocyclic amines, such as pyrazine, pyridazine and pyrimidine. Other catalysts generally include azoles, imidazoles, indoles, oxazoles, thiazoles, substituted species and complex multi-ring amines such as adenine, pterin, pteridine, benzimidazole, phenanthroline and the like.

[0036] Cross sectional area flow rates for the anolyte feed **102** and the catholyte feed **103** may be 2-3,000 gpm/ft² or

more (0.0076-11.36 m³/m²) with a flow velocity range of 0.002 to 20 ft/sec (0.0006 to 6.1 m/sec).

[0037] Operating the catholyte region **106** at a higher relative operating pressure may allow more CO₂ **115** to dissolve in an aqueous catholyte feed **103**. The electrochemical cell **101** may operate at pressures up to about 20 to 30 psig in a multi-cell stack design, although with modifications, the electrochemical cell **101** may operate at up to 100 psig. The anolyte region **105** would also need to be operated in a similar pressure range to minimize the pressure differential on the separator **107** separating the anolyte region **105** and the catholyte region **106**. Special electrochemical designs may be required to operate electrochemical units at higher operating pressures up to about 60 to 100 atmospheres or greater, which is in the liquid CO₂ and supercritical CO₂ operating range.

[0038] In another example embodiment, a portion of a catholyte recycle stream may be separately pressurized using a flow restriction with backpressure or using a pump, with CO₂ injection, such that the pressurized stream may be injected into the catholyte region **106** of the electrochemical cell **101** thereby increasing the amount of dissolved CO₂ in the aqueous solution to improve the conversion yield.

[0039] The catholyte may be operated at a temperature range of -10 to 95 ° C., more preferably 5-60° C. The lower temperature will be limited by the catholytes used and their freezing points. In general, the lower the temperature, the higher the solubility of CO₂ in the aqueous solution phase of the catholyte, and would help in obtaining higher conversion and current efficiencies. The drawback is that the operating electrochemical cell voltages may be higher, so there is an optimization that would be done to produce the chemicals at the lowest operating cost. In addition, the catholyte may require cooling, so an external heat exchanger may be employed, flowing the catholyte through the heat exchanger and using cooling water to remove the heat and control the catholyte temperature.

[0040] The anolyte operating temperatures may be in the same ranges as the ranges for the catholyte, and may be in a range of 0° C. to 95° C. In addition, the anolyte may require cooling, so an external heat exchanger may be employed, flowing the anolyte through the heat exchanger and using cooling water to remove the heat and control the anolyte temperature.

[0041] The electrochemical cell **101** may be configured with zero-gap, flow-through with a recirculating catholyte feed **103** with various high surface area cathode **109** materials. More specifically, the electrochemical cell **101** may be configured with flooded co-current packed and/or trickle bed designs with the various high surface area cathode materials may be used. Further, bipolar stack electrochemical cell designs and high pressure cell designs may be employed

[0042] The anode **108** may include an anode coating. The anode coating may include: precious metal oxides such as ruthenium and iridium oxides, as well as platinum and gold and their combinations as metals and oxides on valve metal substrates such as titanium, tantalum, vanadium, and/or niobium. For other anolyte feeds **102** such as those operating in alkaline or hydroxide anolytes the anode material and anode coating may include: carbon, cobalt oxides, stainless steels, nickel and nickel alloys, other transition metals and their alloys and combinations which are stable as anodes.

[0043] Anodes may include electrocatalytic coatings applied to the surfaces of the base anode structure. For example, for HBr, acid anolytes and oxidizing water gener-

ating oxygen, the preferred electrocatalytic coatings may include precious metal oxides such as ruthenium and iridium oxides, as well as platinum and gold and their combinations as metals and oxides on valve metal substrates such as titanium, tantalum, zirconium, or niobium. For bromine and iodine anode chemistry, carbon and graphite are particularly suitable for use as anodes. Polymeric bonded carbon materials may also be used. For other anolytes comprising alkaline or hydroxide electrolytes, anodes may include carbon, cobalt oxides, stainless steels, transition metals, and their alloys and combinations. High surface area anode structures that may be used which would help promote the reactions at the anode surfaces. The high surface area anode base material may be in a reticulated form composed of fibers, sintered powder, sintered screens, and the like, and may be sintered, welded, or mechanically connected to a current distributor back plate that is commonly used in bipolar cell assemblies. In addition, the high surface area reticulated anode structure may also contain areas where additional applied catalysts on and near the electrocatalytic active surfaces of the anode surface structure to enhance and promote reactions that may occur in the bulk solution away from the anode surface such as the reaction between bromine and the carbon based reactant being introduced into the anolyte. The anode structure may be graded, so that the density of the may vary in the vertical or horizontal direction to allow the easier escape of gases from the anode structure. In this gradation, there may be a distribution of particles of materials mixed in the anode structure that may contain catalysts for bulk reactions.

[0044] The separator **107** may be configured as a cation ion exchange-type membrane. Specifically, the separator **107** may be configured to have a high rejection efficiency to anions and high rejection for alcohols. For example, the separator **107** may be a perfluorinated sulfonic acid based ion exchange membranes such as DuPont Nafion® brand unreinforced types N117 and N120 series or PTFE fiber reinforced N324 and N424 types, and similar related membranes manufactured the supplier trade names as Flemion®.

[0045] The separator **107** may be a multi-layer perfluorinated ion exchange membranes having a bilayer construction of a sulfonic acid based membrane layer bonded to a carboxylic acid based membrane layer, which efficiently operates with an anolyte and catholyte above a pH of about 2 or higher. For example, the separator **107** may be those sold by DuPont under their Nafion® trademark as the N900 series, such as the N90209, N966, N982, and the 2000 series, such as the N2010, N2020, and N2030 and all of their types and subtypes.

[0046] The separator **107** may be a hydrocarbon based membrane made from various cation ion exchange materials if the anion rejection is not as critical. For example, the separator **107** may be those sold by Sybron under their trade name Ionac®, AGC Engineering (Asahi Glass) under their Selemion® trade name, and Tokuyama Soda among others on the market.

[0047] The separator **107** may be a ceramic-based membrane. For example, the separator **107** may be a sodium superionic conductor (e.g. a “NASICON” having a composition $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$) which is chemically stable over a wide pH range for various chemicals and selectively transports sodium ions, and well as other ceramic based conductive membranes based on titanium oxides, zirconium oxides and yttrium oxides, and beta aluminum oxides. Preferably, the membrane or separator is chemically resistant to the anolyte

and catholyte and operates at temperatures of less than 600 degrees C., and more preferably less than 500 degrees C.

[0048] The membrane may also include a thin layer of proton-conducting metal such as palladium, titanium, or vanadium to prevent crossover of ethanol while allowing conduction of protons to the cathode.

[0049] Referring to FIG. 3, the reaction at the cathode **109** in the catholyte region **106** may produce a reduction product **112** including H_2 which may combined with carbon dioxide. For example, CO_2 **115** cogenerated at the anode **108** (e.g. from oxidation of an alkane, alkene, phenol or aqueous solutions thereof) or, in a case where an oxidized organic product (e.g. ethanol, methanol, ethylene oxide, propylene oxide, etc.) is generated at the anode **108**, an independent carbon dioxide feed **125**, and the reduction product **112** including H_2 may be fed to a reverse water gas shift reactor **116** which may perform a reverse water gas shift reaction. This reverse water gas shift reaction performed by reverse water gas shift reactor **116** may produce water **117** and carbon monoxide **118**. The carbon monoxide **118** along with the reduction product **112** including H_2 may be combined at reactor **119**. The reactor **119** may cause a reaction, such as a Fischer-Tropsch synthesis reaction, to reduce carbon monoxide to a product **120** including one or more of methane, methanol, hydrocarbons, glycols and/or olefins by utilizing the H_2 reduction product **112** from the reaction at the cathode **109** in the catholyte region **106**.

[0050] Referring to FIG. 4, the reaction at the cathode **109** in the catholyte region **106** may produce reduction product **112** including carbon monoxide may be combined with water **121** in a water gas shift reactor **122** which may perform a water gas shift reaction. This water gas shift reaction performed by reactor **122** may produce CO_2 **123** and H_2 **124**. The reduction product **112** including carbon monoxide and H_2 **124** may be combined at a reactor **125**. The reactor **125** may cause a reaction, such as a Fischer-Tropsch synthesis reaction, to reduce carbon monoxide to one or more products **126** such as methane, methanol, hydrocarbons, glycols, olefins by utilizing H_2 **124**. The CO_2 **123** produced by the water gas shift reaction of reactor **122** may be recycled as an input feed to the catholyte region **106**. In a case where CO_2 **115** is cogenerated at the anode **108** and fed to the catholyte region **106**, the CO_2 **123** may be combined with the CO_2 **115**.

[0051] The rate of the generation of reactant formed in the anolyte region from the anode reaction, such as the oxidation of an alkane to a carboxylic acid, is contemplated to be proportional to the applied current to the electrochemical cell. The rate of the input or feed of the carbon based reactant, for example ethane, into the anolyte region should then be fed in proportion to the generated anode reactant. The molar ratio of the carbon based reactant to the generated anode reactant may be in the range of 100:1 to 1:10, and more preferably in the range of 50:1 to 1:5.

[0052] Similarly, the rate of the generation of the formed electrochemical carbon dioxide reduction product in the catholyte region, such as CO , is contemplated to be proportional to the applied current to the electrochemical cell. The rate of the input or feed of carbon dioxide into the catholyte region should be fed in a proportion to the applied current. The cathode reaction efficiency would determine the maximum theoretical formation in moles of the carbon dioxide reduction product. It is contemplated that the ratio of carbon dioxide feed to the theoretical moles of potentially formed carbon dioxide reduction product would be in a range of 100:1 to 2:1, and preferably in the range of 50:1 to 5:1, where

the carbon dioxide is in excess of the theoretical required for the cathode reaction. The carbon dioxide excess would then be recycled back to the catholyte region.

[0053] The molar ratio of the carbon based reactant to the generated anode reactant may be in the range of 100:1 to 1:10, and more preferably in the range of 50:1 to 1:5. The anolyte product output in this range can be such that the output stream contains little or no free bromine in the product output to the second product extractor, or it may contain unreacted bromine. The operation of the extractor and its selected separation method, may use for example, fractional distillation, to separate the actual oxidation products.

[0054] In the present disclosure, the methods disclosed may be implemented as sets of instructions or software readable by a device. Further, it is understood that the specific order or hierarchy of steps in the methods disclosed are examples of exemplary approaches. Based upon design preferences, it is understood that the specific order or hierarchy of steps in the method can be rearranged while remaining within the disclosed subject matter. The accompanying method claims present elements of the various steps in a sample order, and are not necessarily meant to be limited to the specific order or hierarchy presented.

[0055] 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 without departing from the disclosed subject matter or without sacrificing all of its material advantages. The form described is merely explanatory, and it is the intention of the following claims to encompass and include such changes.

1-6. (canceled)

7. A system for at least partially simultaneously electrochemically generating an oxidation product and a reduction product, the system comprising:

- an electrochemical cell including an anolyte region and a catholyte region separated by at least one ion exchange membrane;
- an organic compound feed input operably coupled to the anolyte region; and a carbon dioxide feed input operably coupled to the catholyte region.

8. The system of claim 7, further comprising:

- a gas/fluid coupling between the anolyte region and the catholyte region and configured for the transfer of carbon dioxide generated in an oxidation reaction in the anolyte region to the catholyte region.

9. The system of claim 7, wherein an organic compound feed to the anolyte region includes an aqueous solution of an organic compound.

10. The system of claim 7, wherein an organic compound feed to the anolyte region includes a compound feed selected from at least one of: an alkane, an alkene; an aromatic; a carboxylic acid; an aldehyde; a ketone; an alcohol; a cyanide; a phenol, a sugar, a glycol, a surfactant, and a halogenated organic compound.

11. The system of claim 7, where a reduction product generated in the catholyte region is selected from at least one of: hydrogen, carbon monoxide, carbon, formic acid, formaldehyde, methanol, methane, oxalate, oxalic acid, glyoxylic acid, glyoxylate, glycolic acid, glycolate, glyoxal, glycolaldehyde, ethylene glycol, acetic acid, acetate, acetaldehyde, ethanol, ethane, ethylene, lactic acid, lactate, propanoic acid, propionate, acetone, isopropanol, 1-propanol, 1,2-propylene

glycol, propane, propylene, butane, butene, 1-butanol, 2-butanone, 2-butanol, a carboxylic acid, a carboxylate, an aldehyde, and a ketone.

12. The system of claim 7, wherein an anode of the anolyte region includes an electrocatalyst including at least one of lead dioxide, tin oxides, conductive titanium sub-oxides and boron doped diamond.

13. A method for at least partially simultaneously electrochemically generating carbon dioxide, an oxidation product and a reduction product, the method comprising:

- receiving a feed of at least one organic compound into an anolyte region of an electrochemical cell;
- at least partially oxidizing the at least one organic compound to generate at least carbon dioxide and at least one oxidation product;
- receiving at least one feed including carbon dioxide into a catholyte region of the electrochemical cell including a cathode
- at least partially reducing carbon dioxide received in the catholyte region to generate at least one reduction product.

14. The method of claim 13, wherein the feed including carbon dioxide includes at least one of carbon dioxide generated at the anode and a supplemental feed including carbon dioxide.

15. The method of claim 13, wherein the at least one oxidation product is selected from at least one of: a carboxylic acid; an organic acid; a cyanate, a carbonate, a compound including nitrogen, an oxide, a ketone, an alcohol, an aldehyde, and a de-halogenated compound.

16. The method of claim 13, where the reduction product is selected from at least one of: hydrogen, carbon monoxide, formic acid, formaldehyde, methanol, methane, oxalate, oxalic acid, glyoxylic acid, glyoxylate, glycolic acid, glycolate, glyoxal, glycolaldehyde, ethylene glycol, acetic acid, acetate, acetaldehyde, ethanol, ethane, ethylene, lactic acid, lactate, propanoic acid, propionate, acetone, isopropanol, 1-propanol, 1,2-propylene glycol, propane, propylene, 1-butanol, 2-butanone, butane, butene, 2-butanol a carboxylic acid, a carboxylate, an aldehyde, and a ketone.

17. The method of claim 13, wherein the at least one reduction product includes at least one C₁ to C₄ reduction product.

18. A method for simultaneously electrochemically generating an oxidation product and a reduction product, the method comprising:

- receiving a feed of at least one organic compound into an anolyte region of an electrochemical cell;
- at least partially oxidizing the at least one organic compound to generate at least one oxidation product;
- receiving a feed including carbon dioxide into a catholyte region of the electrochemical cell; and
- at least partially reducing the carbon dioxide to generate at least one reduction product.

19. The method of claim 18, wherein the at least one organic compound is selected from at least one of: an alkane, an alkene; an aromatic; a carboxylic acid; an aldehyde; a ketone; an alcohol; a cyanide; a phenol, a sugar, a glycol, a surfactant, and a halogenated organic compound.

20. The method of claim 18, wherein the at least one oxidation product is selected from at least one of: a carboxylic acid; an organic acid; a cyanate, a carbonate, a nitrogen compound, an oxide, an alcohol, a ketone, an aldehyde, and a de-halogenated compound.

21. The method of claim **18**, where the at least one reduction product is selected from at least one of: hydrogen, carbon monoxide, formic acid, formaldehyde, methanol, methane, oxalate, oxalic acid, glyoxylic acid, glyoxylate, glycolic acid, glycolate, glyoxal, glycolaldehyde, ethylene glycol, acetic acid, acetate, acetaldehyde, ethanol, ethane, ethylene, lactic acid, lactate, propanoic acid, propionate, acetone, isopropanol, 1-propanol, 1,2-propylene glycol, propane, propylene, 1-butanol, 2-butanone, butane, butene, 2-butanol a carboxylic acid, a carboxylate, an aldehyde, and a ketone.

22. The method of claim **18**, wherein the anolyte region of the electrochemical cell includes an at least partially solution phase.

23. The method of claim **22**, wherein the organic compound includes at least benzene in the solution phase.

24. The method of claim **23**, wherein the at least one oxidation product is phenol.

25. The method of claim **18**, wherein the anolyte region of the electrochemical cell includes an at least partially gaseous phase.

26. The method of claim **25**, wherein the gaseous phase includes water vapor.

27. The method of claim **26**,
wherein the gaseous phase further includes at least one of
an alkane and an alkene; and
wherein the at least one oxidation product is at least one of
an alcohol and an oxide.

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