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(54) Title: REDUCING CARBON DIOXIDE TO PRODUCTS

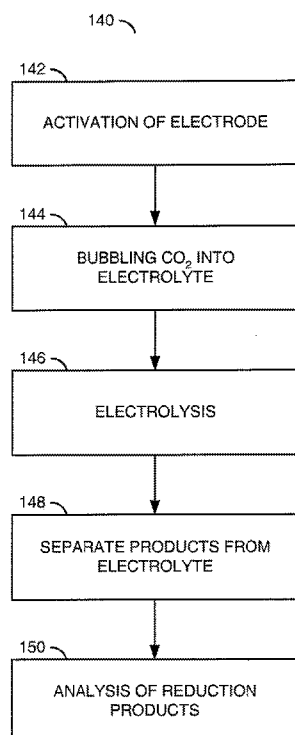


FIG. 7

(57) Abstract: A method for reducing carbon dioxide to one or more products is disclosed. The method may include steps (A) to (C). Step (A) may bubble the carbon dioxide into a solution of an electrolyte and a catalyst in a divided electrochemical cell. The divided electrochemical cell may include an anode in a first cell compartment and a cathode in a second cell compartment. The cathode generally reduces the carbon dioxide into the products. Step {B} may vary at least one of (i) which of the products is produced and (ii) a faradaic yield of the products by adjusting one or more of (a) a cathode material and (b) a surface morphology of the cathode. Step (C) may separate the products from the solution.



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REDUCING CARBON DIOXIDE TO PRODUCTS

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Field of the Invention

The present invention relates to chemical reduction generally and, more particularly, to a method and/or apparatus for implementing reducing carbon dioxide to products.

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Background of the Invention

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The combustion of fossil fuels in activities such as the 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.

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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 will be possible. Electrochemical

and photochemical pathways are means for the carbon dioxide conversion.

Previous work in the field has many limitations, including the stability of systems used in the process, the efficiency of systems, the selectivity of the systems or processes for a desired chemical, the cost of materials used in systems/processes, the ability to control the processes effectively, and the rate at which carbon dioxide is converted. No commercially available solutions for converting carbon dioxide to economically valuable fuels or industrial chemicals currently exist. Laboratories around the world have attempted for many years to use electrochemistry and/or photochemistry to convert carbon dioxide to economically valuable products. Hundreds of publications exist on the subject, starting with work in the 19th century. Much of the work done prior to 1999 is summarized in "Greenhouse Gas Carbon Dioxide Mitigation Science and Technology", by Halmann and Steinberg. A more recent overview of work on electrochemical means of reducing carbon dioxide is "Electrochemical Carbon Dioxide Reduction - Fundamental and Applied Topics (Review)", by Maria Jitaru in Journal of the University of Chemical Technology and Metallurgy, 2007, pages 333-344.

Laboratory electrochemical methods usually involve a small (i.e., <1 liter) glass cell containing electrodes and an aqueous solution with supporting electrolyte in which carbon dioxide is bubbled, though a solvent other than water can be used. Reduction of the carbon dioxide takes place directly on the cathode or via a mediator in the solution that is either a transition metal or a transition metal complex. Photoelectrochemical methods also incorporate aqueous solutions with supporting electrolyte in which carbon dioxide is bubbled. The main difference is that some or all

of the energy for reducing the carbon dioxide comes from sunlight. The reduction of the carbon dioxide takes place on a photovoltaic material or on a catalyst photosensitized by a dye. All systems developed to date have failed to make commercial systems for the reasons outlined above. The systems developed in laboratories could not be scaled to commercial or industrial size because of various performance limitations.

Existing electrochemical and photochemical processes/systems have one or more of the following problems that prevent commercialization on a large scale. Several processes utilize metals such as ruthenium or gold that are rare and expensive. In other processes, organic solvents were used that made scaling the process difficult because of the costs and availability of the solvents, such as dimethyl sulfoxide, acetonitrile and propylene carbonate. Copper, silver and gold have been found to reduce carbon dioxide to various products. However, the electrodes are quickly "poisoned" by undesirable reactions on the electrode and often cease to work in less than an hour. Similarly, gallium-based semiconductors reduce carbon dioxide, but rapidly dissolve in water. Many cathodes make a mix of organic products. For instance, copper produces a mix of gases and liquids including carbon monoxide, methane, formic acid, ethylene and ethanol. A mix of products makes extraction and purification of the products costly and can result in undesirable waste products that must be disposed. Much of the work done to date on carbon dioxide reduction is inefficient because of high electrical potentials utilized, low faradaic yields of desired products and/or high pressure operation. The energy consumed for reducing carbon dioxide thus becomes prohibitive. Many conventional carbon dioxide reduction techniques have very low rates of reaction. For example,

some commercial systems have current densities in excess of 100 milliamperes per centimeter squared (mA/cm^2), while rates achieved in the laboratory are orders of magnitude less.

5 **Summary of the Invention**

 The present invention concerns a method for reducing carbon dioxide to one or more products. The method may include steps (A) to (C). Step (A) may bubble the carbon dioxide into a solution of an electrolyte and a catalyst in a divided
10 electrochemical cell. The divided electrochemical cell may include an anode in a first cell compartment and a cathode in a second cell compartment. The cathode generally reduces the carbon dioxide into the products. Step (B) may vary at least one of (i) which of the products is produced and (ii) a faradaic yield of the products by
15 adjusting one or more of (a) a cathode material and (b) a surface morphology of the cathode. Step (C) may separate the products from the solution.

 The objects, features and advantages of the present invention include providing a method and/or apparatus for
20 implementing reducing carbon dioxide to products that may (i) catalytically reduce carbon dioxide using steel cathodes or other low cost cathode materials, (ii) produce high faradaic yields (e.g., >20%), (iii) produce organic products with steel and nickel alloy cathodes at ambient temperature and pressure, (iv) provide
25 stable long-term reduction of carbon dioxide using copper-based alloy electrodes and/or (v) provide for commercialization of electrochemical carbon dioxide reduction.

Brief Description of the Drawings

These and other objects, features and advantages of the present invention will be apparent from the following detailed description and the appended claims and drawings in which:

5 FIG. 1 is a block diagram of a system in accordance with a preferred embodiment of the present invention;

 FIGS. 2A-2C are tables illustrating relative product yields for different cathode material, catalyst, electrolyte and pH level combinations;

10 FIG. 3 is a formula of an aromatic heterocyclic amine catalyst;

 FIGS. 4-6 are formulae of substituted or unsubstituted aromatic 5-member heterocyclic amines or 6-member heterocyclic amines;

15 FIG. 7 is a flow diagram of an example method used in electrochemical examples; and

 FIG. 8 is a flow diagram of an example method used in photochemical examples.

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Detailed Description of the Preferred Embodiments

In accordance with some embodiments of the present invention, an electro-catalytic system is provided that generally allows carbon dioxide to be converted at modest overpotentials to highly reduced species in an aqueous solution. Some embodiments generally relate to simple, efficient and economical conversion of carbon dioxide to reduced organic products, such as methanol, formic acid and formaldehyde. Inorganic products such as polymers may also be formed. Carbon-carbon bonds and/or carbon-hydrogen bonds may be formed in the aqueous solution under mild conditions

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utilizing a minimum of energy. In some embodiments, the energy used by the system may be generated from an alternative energy source or directly using visible light, depending on how the system is implemented.

5 The reduction of carbon dioxide may be suitably catalyzed by aromatic heterocyclic amines (e.g., pyridine, imidazole and substituted derivatives). Simple organic compounds have been found to be effective and stable homogenous electrocatalysts and photoelectrocatalysts for the aqueous multiple electron, multiple
10 proton reduction of carbon dioxide to organic products, such as formic acid, formaldehyde and methanol. For production of methanol, the reduction of carbon dioxide may proceed along a 6 electron (e-) transfer pathway. High faradaic yields for the reduced products have generally been found in both electrochemical
15 and photoelectrochemical systems at low reaction overpotentials.

 Metal-derived multi-electron transfer was previously thought to achieve highly reduced products such as methanol. Currently, simple aromatic heterocyclic amine molecules may be capable of producing many different chemical species on route to
20 methanol through multiple electron transfers, instead of metal-based multi-electron transfers.

 Some embodiments of the present invention thus relate to environmentally beneficial methods for reducing carbon dioxide. The methods generally include electrochemically and/or
25 photoelectrochemically reducing the carbon dioxide in an aqueous, electrolyte-supported divided electrochemical cell that includes an anode (e.g., an inert conductive counter electrode) in a cell compartment and a conductive or p-type semiconductor working cathode electrode in another cell compartment. A catalyst may be
30 included to produce a reduced product. Carbon dioxide may be

continuously bubbled through the cathode electrolyte solution to saturate the solution.

For electrochemical reductions, the electrode may be a suitable conductive electrode, such as Al, Au, Ag, C, Cd, Co, Cr, Cu, Cu alloys (e.g., brass and bronze), Ga, Hg, In, Mo, Nb, Ni, Ni alloys, Ni-Fe alloys, Sn, Sn alloys, Ti, V, W, Zn, stainless steel (SS), austenitic steel, ferritic steel, duplex steel, martensitic steel, Nichrome, elgiloy (e.g., Co-Ni-Cr), degenerately doped p-Si, degenerately doped p-Si:As and degenerately doped p-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. Other semiconductor electrodes may be implemented to meet the criteria of a particular application.

The catalyst for conversion of carbon dioxide electrochemically or photoelectrochemically may be a substituted or unsubstituted aromatic heterocyclic amine. Suitable amines are generally heterocycles which may include, but are not limited to, heterocyclic compounds that are 5-member or 6-member rings with at least one ring nitrogen. For example, pyridines, imidazoles and related species with at least one five-member ring, bipyridines (e.g., two connected pyridines) and substituted derivatives were generally found suitable as catalysts for the electrochemical reduction and/or the photoelectrochemical reduction. Amines that have sulfur or oxygen in the rings may also be suitable for the reductions. Amines with sulfur or oxygen may include thiazoles or oxazoles. Other aromatic amines (e.g., quinolines, adenine, azoles, indoles, benzimidazole and 1,10-phenanthroline) may also be effective electrocatalysts.

Carbon dioxide may be photochemically or electrochemically reduced to formic acid with formaldehyde and methanol being formed in smaller amounts. Catalytic hydrogenation of carbon dioxide using heterogeneous catalysts generally provides methanol together with water as well as formic acid and formaldehyde. The reduction of carbon dioxide to methanol with complex metal hydrides, such as lithium aluminum hydrides, may be costly and therefore problematic for bulk production of methanol. Current reduction processes are generally highly energy-consuming and thus are not efficient ways for a high yield, economical conversion of carbon dioxide to various products.

On the other hand, the use of processes for converting carbon dioxide to reduced organic and/or inorganic products in accordance with some embodiments of the invention generally has the potential to lead to a significant reduction of carbon dioxide, a major greenhouse gas, in the atmosphere and thus to the mitigation of global warming. Moreover, some embodiments may advantageously produce methanol and related products without adding extra reactants, such as a hydrogen source. The resultant product mixture may use little in the way of further treatment. For example, a resultant 1 molar (M) methanol solution may be used directly in a fuel cell. For other uses, simple removal of the electrolyte salt and water may be readily accomplished.

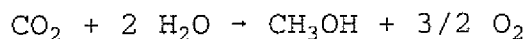
Before any embodiments of the invention are explained in detail, it is to be understood that the embodiments may not be limited in application per the details of the structure or the function as set forth in the following descriptions or illustrated in the figures of the drawing. Different embodiments 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.

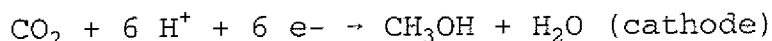
In the following description of methods, process steps may be carried out over a range of temperatures (e.g., approximately 10°C (Celsius) to 50°C) and a range of pressures (e.g., approximately 1 to 10 atmospheres) unless otherwise specified. Numerical ranges recited herein generally include all values from the lower value to the upper value (e.g., all possible combinations of numerical values between the lowest value and the highest value enumerated are considered expressly stated). For example, if a concentration range or beneficial effect range is stated as 1% to 50%, it is intended that values such as 2% to 40%, 10% to 30%, or 1% to 3%, etc., are expressly enumerated. The above may be simple examples of what is specifically intended.

A use of electrochemical or photoelectrochemical reduction of carbon dioxide, tailored with certain electrocatalysts, may produce methanol and related products in a high yield of about 60% to about 100%, based on the amount of carbon dioxide, suitably about 75% to 90%, and more suitably about 85% to 95%. At an electric potential of about -0.50 to -2 volts (V) with respect to a saturated calomel electrode (SCE), methanol may be produced with good faradaic efficiency at the cathode.

An example of an overall reaction for the reduction of carbon dioxide may be represented as follows:



For a 6 e⁻ reduction, the reactions at the cathode and anode may be represented as follows:



5 The reduction of the carbon dioxide may be suitably achieved efficiently in a divided electrochemical or photoelectrochemical cell in which (i) a compartment contains an anode that is an inert counter electrode and (ii) another compartment contains a working cathode electrode and a catalyst.
10 The compartments may be separated by a porous glass frit or other ion conducting bridge. Both compartments generally contain an aqueous solution of an electrolyte. Carbon dioxide gas may be continuously bubbled through the cathodic electrolyte solution to saturate the solution.

15 In the working electrode compartment, carbon dioxide may be continuously bubbled through the solution. In some embodiments, if the working electrode is a conductor, an external bias may be impressed across the cell such that the potential of the working electrode is held constant. In other embodiments, if the working
20 electrode is a p-type semiconductor, the electrode may be suitably illuminated with light. An energy of the light may be matching or greater than a bandgap of the semiconductor during the electrolysis. Furthermore, either no external source of electrical energy may be used or a modest bias (e.g., about 500 millivolts)
25 may be applied. The working electrode potential is generally held constant relative to the SCE. The electrical energy for the electrochemical reduction of carbon dioxide may come from a normal energy source, including nuclear and alternatives (e.g., hydroelectric, wind, solar power, geothermal, etc.), from a solar
30 cell or other nonfossil fuel source of electricity, provided that

the electrical source supply at least 1.6 volts across the cell. Other voltage values may be adjusted depending on the internal resistance of the cell employed.

Advantageously, the carbon dioxide may be obtained from any sources (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 nearly pure carbon dioxide may be exhausted from cement factories and from fermenters used for industrial fermentation of ethanol. 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. Separation of the carbon dioxide from such exhausts is known. 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 unlimited source of carbon.

For electrochemical conversions, the carbon dioxide may be readily reduced in an aqueous medium with a conductive electrode. Faradaic efficiencies have been found high, some reaching about 100%. For photoelectrochemical conversions, the carbon dioxide may be readily reduced with a p-type semiconductor electrode, such as p-GaP, p-GaAs, p-InP, p-InN, p-WSe₂, p-CdTe, p-GaInP₂ and p-Si.

The electrochemical/photoelectrochemical reduction of the carbon dioxide generally utilizes one or more catalysts in the aqueous solution. Aromatic heterocyclic amines 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.

Referring to FIG. 1, a block diagram of a system 100 is shown in accordance with a preferred embodiment of the present invention. The system (or apparatus) 100 generally comprises a cell (or container) 102, a liquid source 104, a power source 106, a gas source 108, an extractor 110 and an extractor 112. A product may be presented from the extractor 110. An output gas may be presented from the extractor 112. Another output gas may be presented from the cell 102.

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

reduce carbon dioxide (CO₂) and protons into one or more organic products and/or inorganic products. The reduction generally takes place by bubbling carbon dioxide into an aqueous solution of an electrolyte in the cell 102. A cathode in the cell 102 may reduce the carbon dioxide into one or more compounds.

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. An aqueous solution 122 may fill both compartments 114a-114b. A catalyst 124 may be added to the compartment 114b containing the cathode 120.

The liquid source 104 may implement a water source. The liquid source 104 may be operational to provide pure water to the cell 102.

The power source 106 may implement a variable voltage source. The 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.

The gas source 108 may implement a carbon dioxide source. The source 108 is generally operational to provide carbon dioxide to the cell 102. In some embodiments, the carbon dioxide is bubbled directly into the compartment 114b containing the cathode 120.

The extractor 110 may implement an organic product and/or inorganic product extractor. The extractor 110 is generally operational to extract (separate) products (e.g., formic acid, acetone, glyoxal, isopropanol, formaldehyde, methanol, polymers and the like) from the electrolyte 122. The extracted products may be

presented through a port 126 of the system 100 for subsequent storage and/or consumption by other devices and/or processes.

The extractor 112 may implement an oxygen extractor. The extractor 112 is generally operational to extract oxygen (e.g., O₂) byproducts created by the reduction of the carbon dioxide and/or the oxidation of water. 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. The organic pollutants may be rendered harmless by oxidization. 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.

In the process described, water may be oxidized (or split) to protons and oxygen at the anode 118 while the carbon dioxide is reduced to organic products at the cathode 120. The electrolyte 122 in the cell 102 may use water as a solvent with any salts that are water soluble and with a pyridine or pyridine-derived catalyst 124. The catalysts 124 may include, but are not limited to, nitrogen, sulfur and oxygen containing heterocycles. Examples of the heterocyclic compounds may be pyridine, imidazole, pyrrole, thiazole, furan, thiophene and the substituted heterocycles such as amino-thiazole and benzimidazole. Cathode materials generally include any conductor. Any anode material may be used. The overall process is generally driven by the power source 106. Combinations of cathodes 120, electrolytes 122, catalysts 124, introduction of carbon dioxide to the cell 102, pH levels and electric potential from the power source 106 may be used to control the reaction products of the cell 102. Organic products and inorganic products resulting from the reaction may

include, but are not limited to, acetaldehyde, acetone, carbon, carbon monoxide, carbonates, ethanol, ethylene, formaldehyde, formic acid, glyoxal, glyoxylic acid, graphite, isopropanol, methane, methanol, oxalate, oxalic acid and/or carbon dioxide containing polymers.

In some nonaqueous embodiments, the solvent may include methanol, acetonitrile, and/or other nonaqueous solvents. The electrolytes 122 generally include tetraalkyl ammonium salts and a heterocyclic catalyst. A primary product may be oxalate in a completely nonaqueous system. In a system containing a nonaqueous catholyte and an aqueous anolyte, the products generally include all of the products seen in aqueous systems with higher yields.

Experiments were conducted in one, two and three-compartment electrochemical cells 102 with an SCE as the reference electrode. The experiments were generally conducted at ambient temperature and pressure. Current densities were observed to increase with increased temperature, but the experiments were generally operated at ambient temperature for best efficiency. Carbon dioxide was bubbled into the cells during the experiments. A potentiostat or DC power supply 106 provided the electrical energy to drive the process. Cell potentials ranged from 2 volts to 4 volts, depending on the cathode material. Half cell potentials at the cathode ranged from -0.7 volts to -2 volts relative to the SCE, depending on the cathode material used. Products from the experiments were analyzed using gas chromatography and a spectrometer.

The process is generally controlled to get a desired product by using combinations of specific cathode materials, catalysts, electrolytes, surface morphology of the electrodes, introduction of reactants relative to the cathode, adjusting pH

levels and/or adjusting electrical potentials. Faradaic yields for the products generally range from less than 1% to more than 90% with the remainder being hydrogen, though methane, carbon monoxide and/or ethylene may also be produced as gaseous byproducts.

5 Referring to FIGS. 2A-2C, tables illustrating relative product yields for different cathode material, catalyst, electrolyte, pH level and cathode potential combinations are shown. The combinations listed in the tables generally are not the only combinations providing a given product. The combinations
10 illustrated may demonstrate high yields of the products at the lowest potential. The cathodes tested generally include all conductive elements on the periodic table, steels, nickel alloys, copper alloys such as brass and bronze and elgiloy. Most of the conductors may be used with heterocyclic catalysts 124 to reduce
15 the carbon dioxide. The products created may vary based on which cathode material is used. For instance, a W cathode 120 with pyridine catalyst 124 may give acetone as a product whereas a Sn cathode 120 with pyridine may primarily give formic acid and methanol as products. A product yield may also be changed by the
20 manner in which the carbon dioxide was bubbled into the cell 102. For instance, with a stainless steel 2205 cathode 120 in a KCl electrolyte 122, if the carbon dioxide bubbles directly hit the cathode 120, the product mix may switch to methanol and isopropanol, rather than formic acid and acetone when the carbon
25 dioxide bubbles miss the cathode 120.

Cell design and cathode treatment (e.g., surface morphology or surface texture) may affect both product yields and current density at the cathode. For instance, a divided cell 102 with a stainless steel 2205 cathode 120 in a KCl electrolyte 122
30 generally has higher yields with a heavily scratched (rough)

cathode 120 than an unscratched (smooth) cathode 120. Matte tin generally performs different than bright tin. Maintaining carbon dioxide bubbling only on the cathode side of the divided cell 102 (e.g., in compartment 114b) may also increase yields.

5 Raising or lowering the cathode potential may also alter the reduced products. For instance, ethanol is generally evolved at lower potentials between -0.8 volts and -1 volt using the duplex steel/pyridine/KCl, while methanol is favored beyond -1 volt.

10 Faradaic yields for the products may be improved by controlling the electrical potential of the reaction. By maintaining a constant potential at the cathode 120, hydrogen evolution is generally reduced and faradaic yields of the products increased. Addition of hydrogen inhibitors, such as acetonitrile, certain heterocycles, alcohols, and other chemicals may also
15 increase yields of the products.

 With some embodiments, stability may be improved with cathode materials known to poison rapidly when reducing carbon dioxide. Copper and copper-alloy electrodes commonly poison in less than an hour of electrochemically reducing carbon dioxide.
20 However, when used with a heterocyclic amine catalyst, copper-based alloys were operated for many hours without any observed degradation in effectiveness. The effects were particularly enhanced by using sulfur containing heterocycles. For instance, a system with a copper cathode and 2-amino thiazole catalyst showed
25 very high stability for the reduction of carbon dioxide to carbon monoxide and formic acid.

 Heterocycles other than pyridine may catalytically reduce carbon dioxide in the electrochemical process using many aforementioned cathode materials, including tin, steels, nickel
30 alloys and copper alloys. Nitrogen-containing heterocyclic amines

shown to be effective include azoles, indoles, 4,4'-bipyridines, picolines (methyl pyridines), lutidines (dimethyl pyridines), hydroxy pyridines, imidazole, benzimidazole, methyl imidazole, pyrazine, pyrimidine, pyridazine, pyridazineimidazole, nicotinic acid, quinoline, adenine and 1,10-phenanthroline. Sulfur containing heterocycles include thiazole, aminothiazoles, thiophene. Oxygen containing heterocycles include furan and oxazole. As with pyridine, the combination of catalyst, cathode material and electrolyte may be used to control product mix.

Some process embodiments of the present invention for making/converting hydrocarbons generally consume a small amount of water (e.g., approximately 1 to 3 moles of water) per mole of carbon. Therefore, the processes may be a few thousand times more water efficient than existing production techniques.

Referring to FIG. 3, a formula of an aromatic heterocyclic amine catalyst is shown. The ring structure may be an aromatic 5-member heterocyclic ring or 6-member heterocyclic ring with at least one ring nitrogen and is optionally substituted at one or more ring positions other than nitrogen with R. L may be C or N. R1 may be H. R2 may be H if L is N or R2 is R if L is C. R is an optional substituent on any ring carbon and may be independently selected from H, a straight chain or branched chain lower alkyl, hydroxyl, amino, pyridyl, or two R's taken together with the ring carbons bonded thereto are a fused six-member aryl ring and n = 0 to 4.

Referring to FIGS. 4-6, formulae of substituted or unsubstituted aromatic 5-member heterocyclic amines or 6-member heterocyclic amines are shown. Referring to FIG. 4, R3 may be H. R4, R5, R7 and R8 are generally independently H, straight chain or branched chain lower alkyl, hydroxyl, amino, or taken together are

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a fused six-member aryl ring. R6 may be H, straight chain or branched chain lower alkyl, hydroxyl, amino or pyridyl.

Referring to FIG. 5, one of L1, L2 and L3 may be N, while the other L's may be C. R9 may be H. If L1 is N, R10 may be H.
5 If L2 is N, R11 may be H. If L3 is N, R12 may be H. If L1, L2 or L3 is C, then R10, R11, R12, R13 and R14 may be independently selected from straight chain or branched chain lower alkyl, hydroxyl, amino, or pyridyl.

Referring to FIG. 6, R15 and R16 may be H. R17, R18 and
10 R19 are generally independently selected from straight chain or branched chain lower alkyl, hydroxyl, amino, or pyridyl.

Suitably, the concentration of aromatic heterocyclic amine catalysts is about 1 millimolar (mM) to 1 M. The electrolyte may be suitably a salt, such as KCl, NaNO₃, Na₂SO₄, NaCl, NaF, NaClO₄, KClO₄, K₂SiO₃, or CaCl₂ at a concentration of about 0.5 M.
15 Other electrolytes may include, but are not limited to, all group 1 cations (e.g., H, Li, Na, K, Rb and Cs) except Francium (Fr), Ca, ammonium cations, alkylammonium cations and alkyl amines. Additional electrolytes may include, but are not limited to, all
20 group 17 anions (e.g., F, Cl, Br, I and At), borates, carbonates, nitrates, nitrites, perchlorates, phosphates, polyphosphates, silicates and sulfates. Na generally performs as well as K with regard to best practices, so NaCl may be exchanged with KCl. NaF may perform about as well as NaCl, so NaF may be exchanged for NaCl
25 or KCl in many cases. Larger anions tend to change the chemistry and favor different products. For instance, sulfate may favor polymer or methanol production while Cl may favor products such as acetone. The pH of the solution is generally maintained at about pH 3 to 8, suitably about 4.7 to 5.6.

At conductive electrodes, formic acid and formaldehyde were found to be intermediate products along the pathway to the 6 e- reduced product of methanol, with an aromatic amine radical (e.g., the pyridinium radical, playing a role in the reduction of both intermediate products). The intermediate products have generally been found to also be the final products of the reduction of carbon dioxide at conductive electrodes or p-type semiconductor electrodes, depending on the particular catalyst used. Other C-C couple products may also be possible. For example, reduction of carbon dioxide may suitably yield formaldehyde, formic acid, glyoxal, methanol, isopropanol, or ethanol, depending on the particular aromatic heterocyclic amine used as the catalyst. The products of the reduction of carbon dioxide are generally substitution-sensitive. As such, the products may be selectively produced. For example, use of 4,4'-bipyridine as the catalyst may produce methanol and/or 2-propanol. Lutidines and amino-substituted pyridines may produce 2-propanol. Hydroxy-pyridine may produce formic acid.

The effective electrochemical/photoelectrochemical reduction of carbon dioxide disclosed herein may provide new methods of producing methanol and other related products in an improved, efficient, and environmentally beneficial way, while mitigating carbon dioxide-caused climate change (e.g., global warming). Moreover, the methanol product of reduction of carbon dioxide may be advantageously used as (1) a convenient energy storage medium, which allows convenient and safe storage and handling, (2) a readily transported and dispensed fuel, including for methanol fuel cells and (3) a feedstock for synthetic hydrocarbons and corresponding products currently obtained from oil and gas resources, including polymers, biopolymers and even

proteins, that may be used for animal feed or human consumption. Importantly, the use of methanol as an energy storage and transportation material generally eliminates many difficulties of using hydrogen for such purposes. The safety and versatility of methanol generally makes the disclosed reduction of carbon dioxide further desirable.

Some embodiments of the present invention may be further explained by the following examples, which should not be construed by way of limiting the scope of the invention.

Example 1: General Electrochemical Methods.

Chemicals and materials. All chemicals used were > 98% purity and used as received from the vendor (e.g., Aldrich), without further purification. Either deionized or high purity water (Nanopure, Barnstead) was used to prepare the aqueous electrolyte solutions.

Electrochemical system. The electrochemical system was composed of a standard two-compartment electrolysis cell to separate the anode and cathode reactions. The compartments were separated by a porous glass frit or other ion conducting bridge. The electrolytes were used at concentrations of 0.1 M to 1 M, with 0.5 M being a typical concentration. A concentration of between about 1 mM to 1 M of the catalysts were used. The particular electrolyte and particular catalyst of each given test were generally selected based upon what product or products were being created.

Referring to FIG. 7, a flow diagram of an example method used in the electrochemical examples is shown. The method (or process) generally comprises a step (or block), a step (or block), a step (or block), a step (or block) and a step

(or block) 150. The method 140 may be implemented using the system 100.

In the step 142, the electrodes 118 and 120 may be activated where appropriate. Bubbling of the carbon dioxide into the cell 102 may be performed in the step 144. Electrolysis of the carbon dioxide into organic and/or inorganic products may occur during step 146. In the step 148, the products may be separated from the electrolyte. Analysis of the reduction products may be performed in the step 150.

The working electrode was of a known area. All potentials were measured with respect to a saturated calomel reference electrode (Accumet). Before and during all electrolysis, carbon dioxide (Airgas) was continuously bubbled through the electrolyte to saturate the solution. The resulting pH of the solution was maintained at about pH 3 to pH 8 with a suitable range depending on what product or products were being made. For example, under constant carbon dioxide bubbling, the pH levels of 10 mM solutions of 4-hydroxy pyridine, pyridine and 4-tertbutyl pyridine were 4.7, 5.28 and 5.55, respectively. For Nuclear Magnetic Resonance (NMR) experiments, isotopically enriched ^{13}C NaHCO_3 (99%) was obtained from Cambridge Isotope Laboratories, Inc.

Example 2: General Photoelectrochemical Methods.

Chemicals and materials. All chemicals used were analytical grade or higher. Either deionized or high purity water (Nanopure, Barnstead) was used to prepare the aqueous electrolyte solutions.

Photoelectrochemical system. The photoelectrochemical system was composed of a Pyrex three-necked flask containing 0.5 M KCl as supporting electrolyte and a 1 mM to 1 M catalyst (e.g., 10 mM pyridine or pyridine derivative). The photocathode was a single

crystal p-type semiconductor etched for approximately 1 to 2 minutes in a bath of concentrated $\text{HNO}_3\text{:HCl}$, 2:1 v/v prior to use. An ohmic contact was made to the back of the freshly etched crystal using an indium/zinc (2 wt. % Zn) solder. The contact was connected to an external lead with conducting silver epoxy (Epoxy Technology H31) covered in glass tubing and insulated using an epoxy cement (Loctite 0151 Hysol) to expose only the front face of the semiconductor to solution. All potentials were referenced against a saturated calomel electrode (Accumet). The three electrode assembly was completed with a carbon rod counter electrode to minimize the reoxidation of reduced carbon dioxide products. During all electrolysis, carbon dioxide gas (Airgas) was continuously bubbled through the electrolyte to saturate the solution. The resulting pH of the solution was maintained at about pH 3 to 8 (e.g., pH 5.2).

Referring to FIG. 8, a flow diagram of an example method 160 used in the photochemical examples is shown. The method (or process) 160 generally comprises a step (or block) 162, a step (or block) 164, a step (or block) 166, a step (or block) 168 and a step (or block) 170. The method 160 may be implemented using the system 100.

In the step 162, the photoelectrode may be activated. Bubbling of the carbon dioxide into the cell 102 may be performed in the step 164. Electrolysis of the carbon dioxide into the products may occur during step 166. In the step 168, the products may be separated from the electrolyte. Analysis of the reduction products may be performed in the step 170.

Light sources. Four different light sources were used for the illumination of the p-type semiconductor electrode. For initial electrolysis experiments, a Hg-Xe arc lamp (USHIO UXM 200H)

was used in a lamp housing (PTI Model A-1010) and powered by a PTI LTS-200 power supply. Similarly, a Xe arc lamp (USHIO UXL 151H) was used in the same housing in conjunction with a PTI monochromator to illuminate the electrode at various specific wavelengths.

A fiber optic spectrometer (Ocean Optics S2000) or a silicon photodetector (Newport 818-SL silicon detector) was used to measure the relative resulting power emitted through the monochromator. The flatband potential was obtained by measurements of the open circuit photovoltage during various irradiation intensities using the 200 watt (W) Hg-Xe lamp ($3 \text{ W/cm}^2 - 23 \text{ W/cm}^2$). The photovoltage was observed to saturate at intensities above approximately 6 W/cm^2 .

For quantum yield determinations, electrolysis was performed under illumination by two different light-emitting diodes (LEDs). A blue LED (Luxeon V Dental Blue, Future Electronics) with a luminous output of 500 milliwatt (mW) $\pm 50 \text{ mW}$ at 465 nanometers (nm) and a 20 nm full width at half maximum (FWHM) was driven at to a maximum rated current of 700 mA using a Xitanium Driver (Advance Transformer Company). A Fraen collimating lens (Future Electronics) was used to direct the output light. The resultant power density that reached the window of the photoelectrochemical cell was determined to be 42 mW/cm^2 , measured using a Scientech 364 thermopile power meter and silicon photodetector. The measured power density was assumed to be greater than the actual power density observed at the semiconductor face due to luminous intensity loss through the solution layer between the wall of the photoelectrochemical cell and the electrode.

Example 3: Analysis of Products of Electrolysis.

Electrochemical experiments were generally performed using a CH Instruments potentiostat or a DC power supply with current logger to run bulk electrolysis experiments. The CH Instruments potentiostat was generally used for cyclic voltammetry. Electrolysis was run under potentiostatic conditions from approximately 6 hours to 30 hours until a relatively similar amount of charge was passed for each run.

Gas Chromatography. The electrolysis samples were analyzed using a gas chromatograph (HP 5890 GC) equipped with a FID detector. Removal of the supporting electrolyte salt was first achieved with an Amberlite IRN-150 ion exchange resin (cleaned prior to use to ensure no organic artifacts by stirring in a 0.1% v/v aqueous solution of Triton X-100, reduced (Aldrich), filtered and rinsed with a copious amount of water, and vacuum dried below the maximum temperature of the resin (approximately 60°C) before the sample was directly injected into the GC which housed a DB-Wax column (Agilent Technologies, 60 m, 1 micrometer (μ m) film thickness). Approximately 1 gram of resin was used to remove the salt from 1 milliliter (mL) of the sample. The injector temperature was held at 200°C, the oven temperature maintained at 120°C, and the detector temperature at 200°C.

Spectrophotometry. The presence of formaldehyde and formic acid was also determined by the chromotropic acid assay. Briefly, a solution of 0.3 g of 4,5-dihydroxynaphthalene-2,7-disulfonic acid, disodium salt dihydrate (Aldrich) was dissolved in 10 mL deionized water before diluting to 100 mL with concentrated sulfuric acid. For formaldehyde, an aliquot of 1.5 mL was then added to 0.5 mL of the sample. The presence of formaldehyde (absorbency at 577 nm) was detected against a standard

curve using an HP 8453 UV-Vis spectrometer. For formic acid, a 0.5 mL aliquot of sample was first reduced with an approximately 100 mg piece of Mg wire and 0.5 mL concentrated hydrochloric acid (added slowly in aliquots over a 10 minute period) to convert to formaldehyde before following the chromotropic acid assay as described above.

Mass spectrometry. Mass spectral data was also collected to identify all organic compounds. In a typical experiment, the sample was directly leaked into an ultrahigh vacuum chamber and analyzed by an attached SRS Residual Gas Analyzer (with the ionizer operating at 70 electron-volts and an emission current of 1 mA). Samples were analyzed against standard methanol spectra obtained at the same settings to ensure comparable fragmentation patterns. Mass spectral data confirmed the presence of methanol and proved that the initial solution before electrolysis contained no reduced CO₂ species. Control experiments also showed that after over 24 hours under illumination the epoxy used to insulate the backside of the electrode did not leach any organic material that would give false results for the reduction of CO₂. NMR spectra of electrolyte volumes after illumination were obtained using an automated Bruker UltrashieldTM 500 Plus spectrometer with an excitation sculpting pulse technique for water suppression. Data processing was achieved using MestReNova software. For methanol standards and electrolyte samples, the representative signal for methanol was observed between 3.18 to 3.30 parts per million (ppm).

Nuclear Magnetic Resonance. NMR spectra of electrolyte volumes after bulk electrolysis were also obtained using an automated Bruker UltrashieldTM 500 Plus spectrometer with an excitation sculpting pulse technique for water suppression. Data processing was achieved using MestReNova software. The

concentrations of formate and methanol present after bulk electrolysis were determined using acetone as the internal standard.

Carbon dioxide may be efficiently converted to value-added products, using either a minimum of electricity (that may be generated from an alternate energy source) or directly using visible light. Some processes described above may generate high energy density fuels that are not fossil-based as well as being chemical feedstock that are not fossil or biologically based. Moreover, the catalysts for the processes may be substituents-sensitive and provide for selectivity of the value-added products.

By way of example, a fixed cathode (e.g., stainless steel 2205) may be used in an electrochemical system where the electrolyte and/or catalyst are altered to change the product mix. In a modular electrochemical system, the cathodes may be swapped out with different materials to change the product mix. In a hybrid photoelectrochemical system, the anode may use different photovoltaic materials to change the product mix.

Some embodiments of the present invention generally provide for new cathode materials, new electrolyte materials and new sulfur and oxygen-containing heterocyclic catalysts. Specific combinations of cathode materials, electrolytes, catalysts, pH levels and/or electrical potentials may be used to get a desired product. The organic products may include, but are not limited to, acetaldehyde, acetone, carbon, carbon monoxide, carbonates, ethanol, ethylene, formaldehyde, formic acid, glyoxal, glyoxylic acid, graphite, isopropanol, methane, methanol, oxalate, oxalic acid. Inorganic products may include, but are not limited to, polymers containing carbon dioxide. Specific process conditions

may be established that maximize the carbon dioxide conversion to specific chemicals beyond methanol.

Cell parameters may be selected to minimize unproductive side reactions like H_2 evolution from water electrolysis. Choice of specific configurations of heterocyclic amine pyridine catalysts with engineered functional groups may be utilized in the system to achieve high faradaic rates. Process conditions described above may facilitate long life (e.g., improved stability), electrode and cell cycling and product recovery. The organic products created may include methanol, formaldehyde, formic acid, glyoxal, acetone, and isopropanol using the same pyridine catalyst with different combinations of electrolytes, cathode materials, bubbling techniques and cell potentials. Heterocyclic amines related to pyridine may be used to improve reaction rates, product yields, cell voltages and/or other aspects of the reaction. Heterocyclic catalysts that contain sulfur or oxygen may also be utilized in the carbon dioxide reduction.

Some embodiments of the present invention may provide cathode and electrolyte combinations for reducing carbon dioxide to products in commercial quantities. Catalytic reduction of carbon dioxide may be achieved using steel or other low cost cathodes. High faradaic yields (e.g., >20%) of organic products with steel and nickel alloy cathodes at ambient temperature and pressure may also be achieved. Copper-based alloys used at the electrodes may remain stable for long-term reduction of carbon dioxide. The relative low cost and abundance of the combinations described above generally opens the possibility of commercialization of electrochemical carbon dioxide reduction.

Various process conditions disclosed above, including cathode materials, cathode surface morphology, electrolyte choice,

catalyst choice, cell voltage, pH level and manner in which the carbon dioxide is bubbled, generally improve control of the reaction so that different products or product mixes may be made. Greater control over the reaction generally opens the possibility for commercial systems that are modular and adaptable to make different products. The new materials and process conditions combinations generally have high faradaic efficiency and relatively low cell potentials, which allows an energy efficient cell to be constructed.

While the invention has been particularly shown and described with reference to the preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made without departing from the scope of the invention.

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CLAIMS

1. A method for reducing carbon dioxide to one or more products, comprising the steps of:

(A) bubbling said carbon dioxide into a solution of an electrolyte and a catalyst in a divided electrochemical cell, wherein (i) said divided electrochemical cell comprises an anode in a first cell compartment and a cathode in a second cell compartment and (ii) said cathode reducing said carbon dioxide into said products;

(B) varying at least one of (i) which of said products is produced and (ii) a faradaic yield of said products by adjusting one or more of (a) a cathode material and (b) a surface morphology of said cathode; and

(C) separating said products from said solution.

2. The method according to claim 1, wherein said cathode material is at least one of Al, Au, Ag, C, Cd, Co, Cr, Cu, Cu alloys, Ga, Hg, In, Mo, Nb, Ni, Ni alloys, Ni-Fe alloys, Sn, Sn alloys, Ti, V, W, Zn, elgiloy, Nichrome, austenitic steel, duplex steel, ferritic steel, martensitic steel, stainless steel, degenerately doped p-Si, degenerately doped p-Si:As and degenerately doped p-Si:B.

3. The method according to claim 1, wherein said surface morphology of said cathode comprises a smooth surface.

4. The method according to claim 1, wherein said surface morphology of said cathode comprises a rough surface.

5. The method according to claim 1, wherein said catalyst is one or more of adenine, amines containing sulfur, amines containing oxygen, azoles, benzimidazole, bipyridines, furan, imidazoles, imidazole related species with at least one
5 five-member ring, indoles, methylimidazole, oxazoles, phenanthroline, pterin, pteridine, pyridines, pyridine related species with at least one six-member ring, pyrrole, quinoline and thiazoles.

6. The method according to claim 1, wherein said products comprise one or more of acetaldehyde, acetone, carbon, carbon monoxide, carbonates, ethanol, ethylene, formaldehyde, formic acid, glyoxal, glyoxylic acid, graphite, isopropanol,
5 methane, methanol, oxalate, oxalic acid and polymers containing carbon dioxide.

7. A method for reducing carbon dioxide to one or more products, comprising the steps of:

(A) bubbling said carbon dioxide into a solution of an electrolyte and a catalyst in a divided electrochemical cell,
5 wherein (i) said divided electrochemical cell comprises an anode in a first cell compartment and a cathode in a second cell compartment and (ii) said cathode reducing said carbon dioxide into said products;

10 (B) varying at least one of (i) which of said products is produced and (ii) a faradaic yield of said products by adjusting one or more of (a) said electrolyte and (b) a manner in which said carbon dioxide is bubbled; and

(C) separating said products from said solution.

8. The method according to claim 7, wherein said electrolyte is at least one of Na_2SO_4 , KCl , NaNO_3 , NaCl , NaF , NaClO_4 , KClO_4 , K_2SiO_3 , CaCl_2 , a H cation, a Li cation, a Na cation, a K cation, a Rb cation, a Cs cation, a Ca cation, an ammonium cation, an alkylammonium cation, a F anion, a Cl anion, a Br anion, an I anion, an At anion, an alkyl amine, borates, carbonates, nitrites, nitrates, phosphates, polyphosphates, perchlorates, silicates, sulfates, and a tetraalkyl ammonium salt.

9. The method according to claim 7, wherein said bubbling comprises the sub-step of:

bubbling said carbon dioxide to hit said cathode.

10. The method according to claim 7, wherein said bubbling comprises the sub-step of:

bubbling said carbon dioxide to miss said cathode.

11. The method according to claim 7, wherein said faradaic yield is at least 20 percent.

12. The method according to claim 7, wherein said cathode comprises a copper-based alloy that remains stable during at least an hour of said reducing.

13. The method according to claim 7, wherein said adjusting includes one or more of (i) a cathode material and (ii) a surface morphology of said cathode.

14. A method for reducing carbon dioxide to one or more products, comprising the steps of:

(A) bubbling said carbon dioxide into a solution of an electrolyte and a catalyst in a divided electrochemical cell, wherein (i) said divided electrochemical cell comprises an anode in a first cell compartment and a cathode in a second cell compartment and (ii) said cathode reducing said carbon dioxide into said products;

(B) varying at least one of (i) which of said products is produced and (ii) a faradaic yield of said products by adjusting one or more of (a) a pH level of said solution and (b) an electrical potential; and

(C) separating said products from said solution.

15. The method according to claim 14, wherein said pH level ranges from approximately 3 to approximately 8.

16. The method according to claim 14, wherein said electrical potential ranges from approximately -0.7 volts to -2 volts.

17. The method according to claim 14, further comprising the step of:

adding to said solution one or more of (i) a hydrogen inhibitor, (ii) a heterocyclic compound and (iii) an alcohol.

18. The method according to claim 14, further comprising the step of:

performing said reducing at ambient temperature and ambient pressure.

19. The method according to claim 14, wherein said cathode comprises steel.

20. The method according to claim 14, wherein said adjusting includes one or more of (i) a cathode material and (ii) a surface morphology of said cathode.

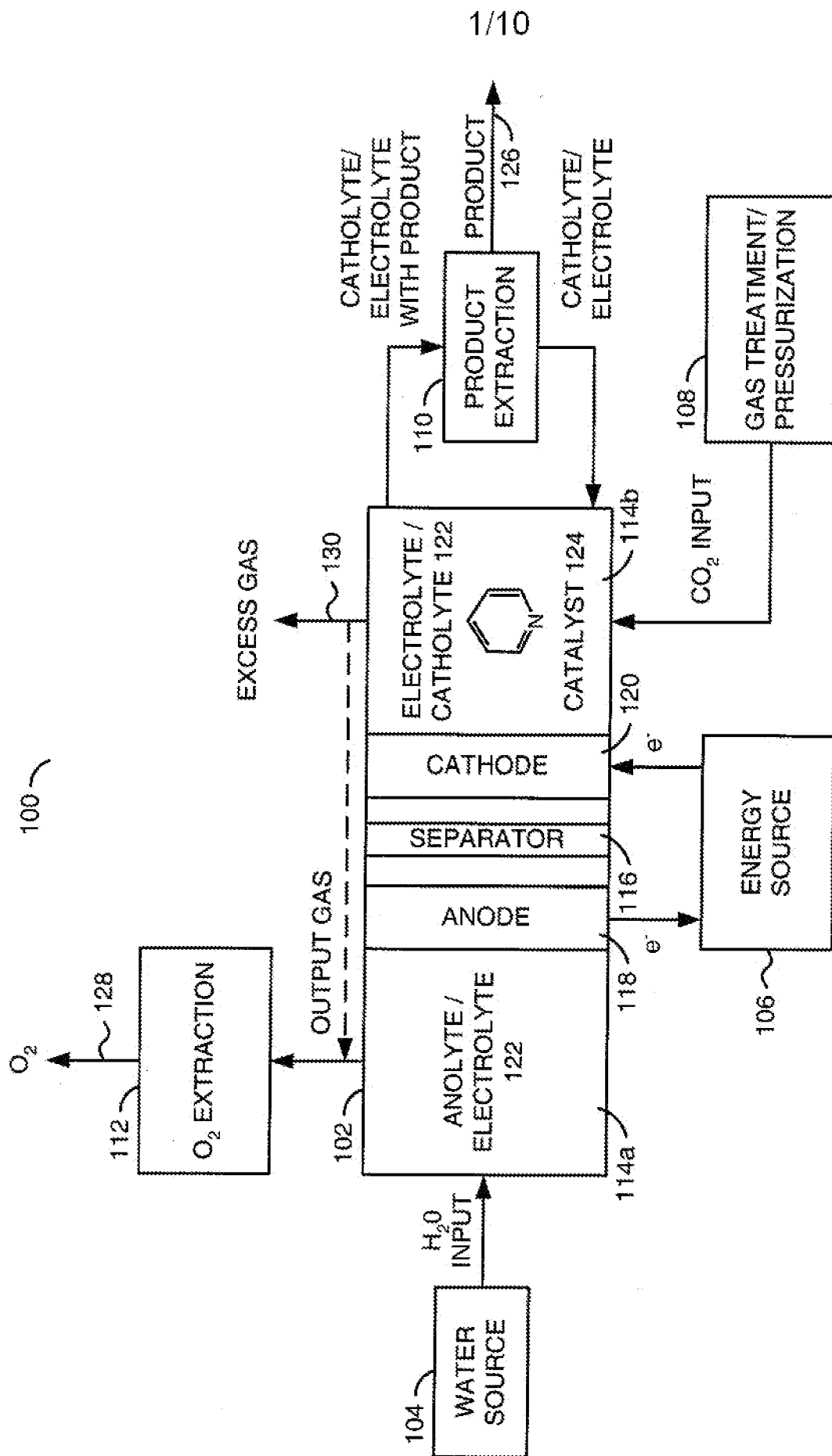


FIG. 1

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PRODUCT	SYSTEM	CATALYST CONCENTRATION	ELECTROLYTE CONCENTRATION	CATHODE POTENTIAL	pH
CARBON MONOXIDE	Sn/PYRIDINE/KCl QUINOLINE ALSO EFFECTIVE	10 TO 100mM	0.25 TO 1M	-1 TO -1.4	5-7
CARBONATE	STEEL/IMIDAZOLE/KCl WITH CaCl ₂	10 TO 100mM	0.5M KCl W/ 0.1M CaCl ₂	-0.9 TO -1.2	4-7
FORMIC ACID	Sn/IMIDAZOLE/KCl OR STAINLESS STEEL/ IMIDAZOLE/CsCl SUBSTITUTED IMIDAZOLES, THIAZOLES, AND ADENINE ALSO EFFECTIVE	10 TO 100mM	0.25 TO 1M	-0.8 TO -1.4	4-8
FORMALDEHYDE	ELGILOY/PYRIDINE/Na ₂ SO ₄	10mM TO 100mM	0.25 TO 1M	-0.8 TO -1.2	4-7
METHANOL	Mo/PYRIDINE/ Na ₂ SO ₄	10mM TO 100mM	0.25 TO 1M	-0.8 TO -1.2	4-7
OXALIC ACID	FERRITIC STEEL/ IMIDAZOLE/CaCl ₂	10mM TO 100mM	0.25 TO 1M	-0.8 TO -1.2	5-7
GLYOXYLIC ACID	FERRITIC STEEL/ IMIDAZOLE/KCl	10mM TO 100mM	0.25 TO 1M	-0.8 TO -1.2	5-7
GLYOXAL	Co/PYRIDINE/KCl	10mM TO 100mM	0.25 TO 1M	-0.8 TO -1.2	5-7
ACETALDEHYDE	Ni ALLOYS/ PYRIDINE/ Na ₂ SO ₄	10mM TO 100mM	0.25 TO 1M	-0.8 TO -1.2	4-7
ETHANOL	DUPLEX STEEL/ IMIDAZOLE/KCl	50mM TO 300mM	0.25 TO 1M	-0.8 TO -1	4-6
ACETONE	DUPLEX STEEL/ PYRIDINE/KCl	10mM TO 100mM	0.25 TO 1M	-0.8 TO -1	4-6
ISOPROPANOL	DUPLEX STEEL/ PYRIDINE/KCl, STAINLESS STEEL/ METHYLIMIDAZOLE/KCl, STAINLESS STEEL/ 2,2' BIPYRIDINE/KCl	10mM TO 100mM	0.25 TO 1M	-0.8 TO -1.2	4-8
POLYMERS	P-Si:As/PYRIDINE/Na ₂ SO ₄	10mM TO 100mM	0.25 TO 1M	-1.6 TO -2	4-8

FIG. 2A

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CATHODE-ELECTROLYTE COMBINATIONS
(WITH 10mM PYRIDINE CATALYST)

CATHODE MATERIAL	ELECTROLYTE	REL YIELD ORGANICS
TIN (Sn)	Na ₂ SO ₄	81% METHANOL, 19% FORMIC ACID
MOLYBDENUM (Mo)	KCl OR Na ₂ SO ₄	100% METHANOL
COBALT (Co)	KCl	36% METHANOL, 74% FORMIC ACID
NICKEL (Ni)	KCl	50% METHANOL, 50% FORMIC ACID
CHROMIUM (Cr)	KCl	100% ACETONE
VANADIUM (V)	KCl	100% METHANOL
NIOBIUM (Nb)	KCl	100% FORMIC ACID
TUNGSTEN (W)	KCl	100% ACETONE
SILVER (Ag)	Na ₂ SO ₄	54% METHANOL, 46% ACETONE
STAINLESS STEEL 304	Na ₂ SO ₄	100% METHANOL
STAINLESS STEEL 316	Na ₂ SO ₄	100% METHANOL
STAINLESS STEEL 316	KCl	100% FORMIC ACID
STAINLESS STEEL 430	KCl	X% GLYOXAL, Y% FORMIC ACID
STAINLESS STEEL 2205	Na ₂ SO ₄	100% METHANOL
STAINLESS STEEL 2205	KCl	UP TO 99% ACETONE, 1% FORMIC ACID
NICHROME (80% Ni, 20% Cr)	KCl	100% ACETONE
Ni-Fe (45% Ni, 55% Fe)	Na ₂ SO ₄	100% METHANOL
NICKEL 625 (INCONEL)	Na ₂ SO ₄	100% METHANOL
NICKEL 625 (INCONEL)	KCl	99% ACETONE, 1% FORMIC ACID

FIG. 2B

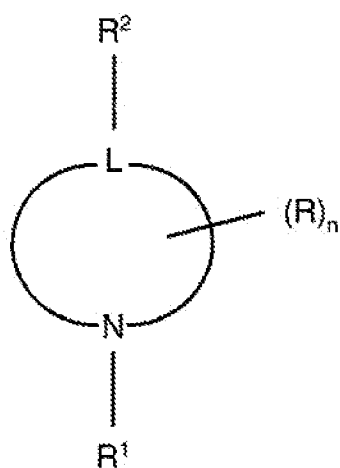
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CATHODE-ELECTROLYTE COMBINATIONS
(WITH 10mM PYRIDINE CATALYST)

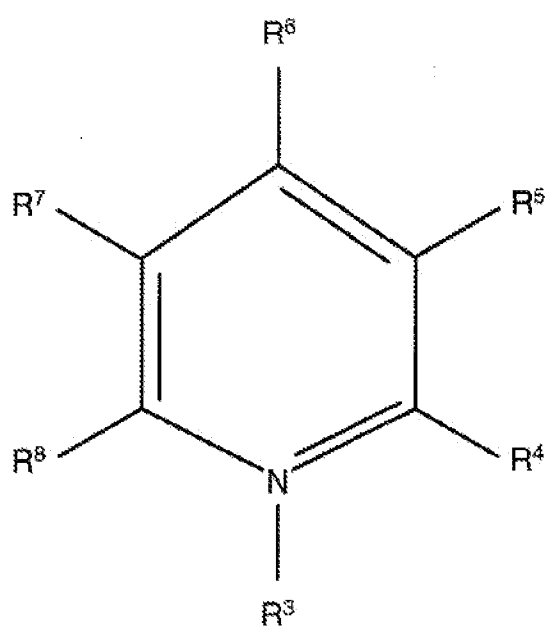
CATHODE MATERIAL	ELECTROLYTE	REL YIELD ORGANICS
NICKEL 600	KCl	55% METHANOL, 45% FORMIC ACID
NICKEL HX	Na ₂ SO ₄	X% GLYOXAL, Y% METHANOL
NICKEL HX	KCl	100% FORMIC ACID
ELGILOY (Co, Ni, Cr)	Na ₂ SO ₄	89% METHANOL, 11% FORMIC ACID
ELGILOY (Co, Ni, Cr)	KCl	95% ACETONE, 5% FORMIC ACID
BRASS 464 (39% Zn)	Na ₂ SO ₄	81% METHANOL, 19% FORMIC ACID
BRONZE 510 (5% Sn)	Na ₂ SO ₄	100% METHANOL
Cu-Mn-Ni	KCl	100% ACETONE
Cu-Ni	KCl	100% ACETONE
BRASS 260	KCl	100% ACETONE

FIG. 2C

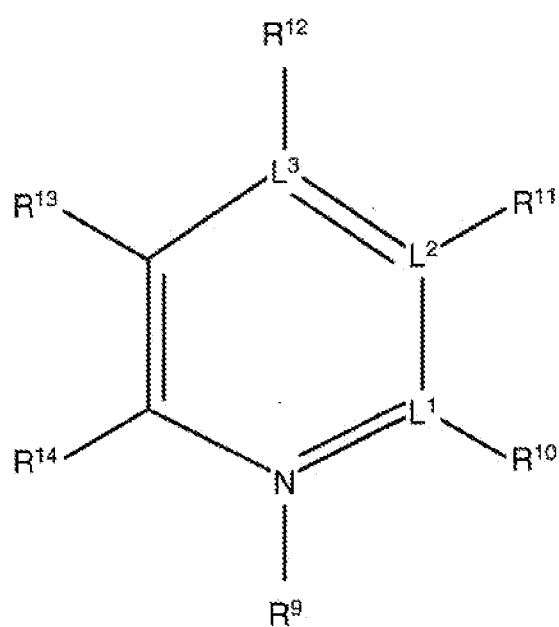
5/10

FIG. 3

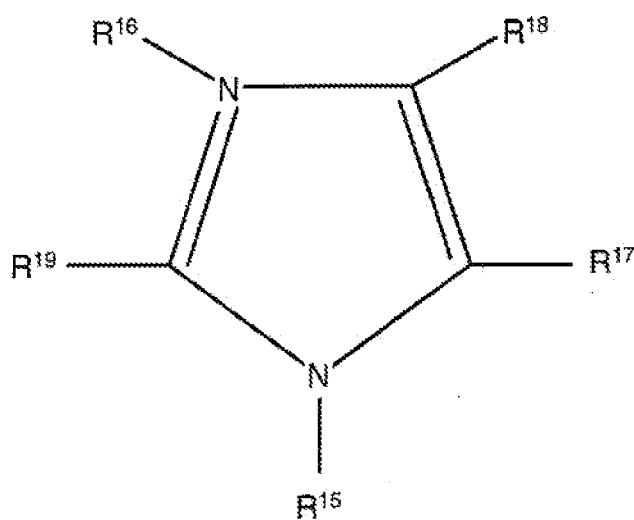
6/10

FIG. 4

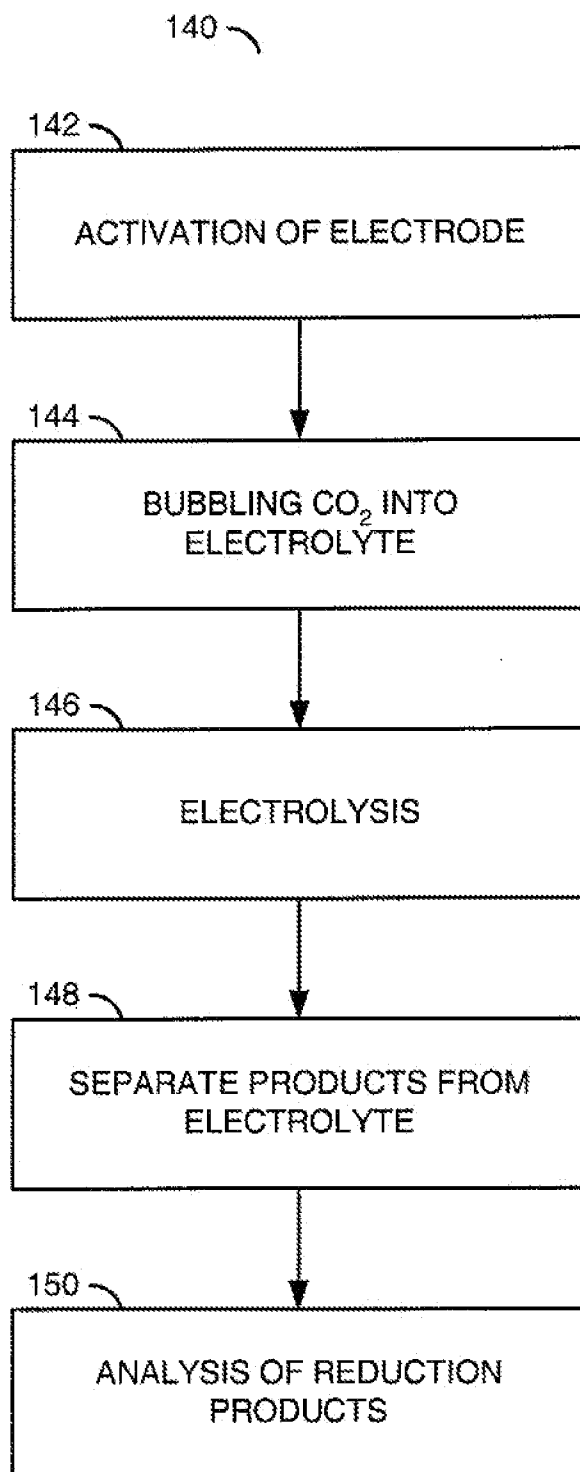
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FIG. 5

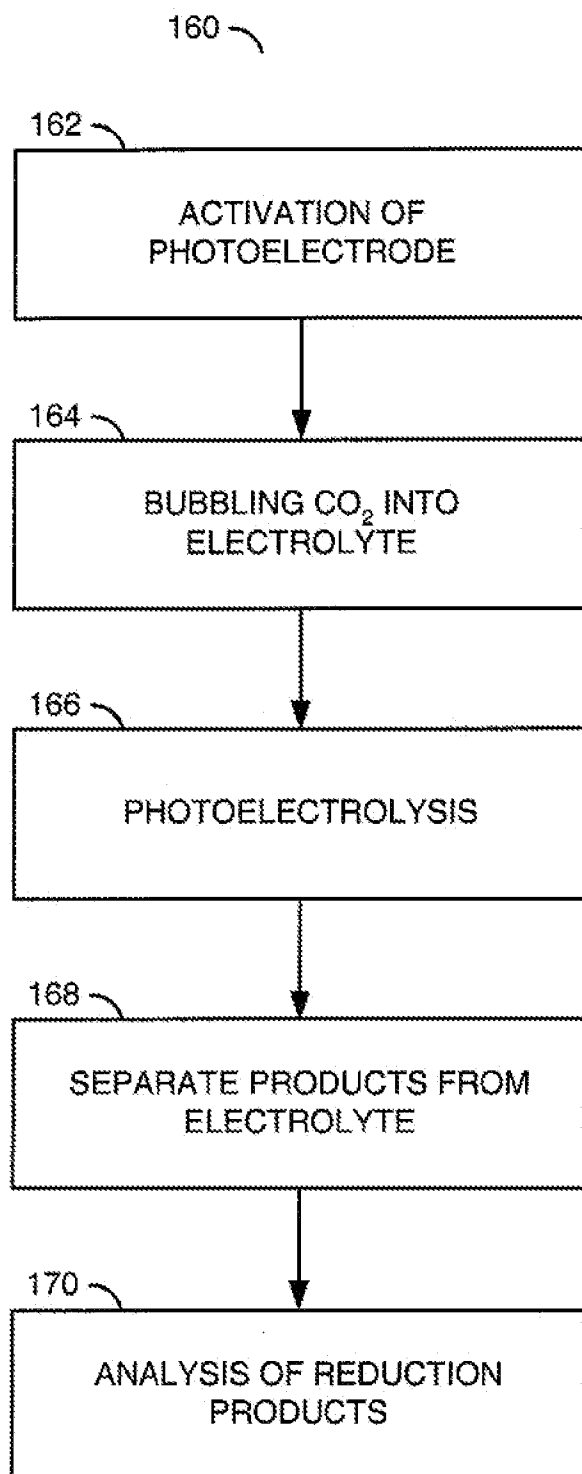
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FIG. 6

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FIG. 7

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FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 11/45515

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C25B 3/04; C25B 1/00 (2011.01)

USPC - 205/414; 205/440; 205/446; 205/448; 205/450

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

USPC -- 205/414; 205/440; 205/446; 205/448; 205/450

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC -- 205/414; 205/440; 205/446; 205/448; 205/450 (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PubWEST (USPT, PGPB, JPAB, EPAB); Google (search terms below)

Search terms used: Carbon dioxide, reduction, electrochemical, anode, cathode, electrolyte, amine, catalyst, textured/rough

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2007/0045125 A1 (Hartvigsen et al.) 01 March 2007 (01.03.2007) entire document especially Abstract, para [0010], [0017], [0056]-[0057], [0055], [0053], [0033] and [0010]	1-20
Y	US 4,897,167 A (Cook et al.) 30 January 1990 (30.01.1990), col 2, ln 43-67; col 5, ln 30-32	1-20
Y	US 2010/0084280 A1 (Gilliam et al.) 08 April 2010 (08.04.2010) entire document especially para [0095]	1-20
Y	US 5,284,563 A (Fujihira et al.) 08 February 1994 (08.02.1994) entire document especially Abstract and col 3, ln 1-30	5
Y	US 5,246,551 A (Pletcher et al.) 21 September 1993 (21.09.1993) entire document especially col 12, ln 36	19

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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