(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 895 642 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
25.04.2018 Bulletin 2018/17

(21) Application number: **13837298.2**

(22) Date of filing: **05.08.2013**

(51) Int Cl.:
C25B 3/04 *(2006.01)* ***C25B 1/04*** *(2006.01)*
C25B 9/08 *(2006.01)* ***C25B 15/08*** *(2006.01)*
C25B 11/03 *(2006.01)* ***C25B 11/04*** *(2006.01)*

(86) International application number:
PCT/US2013/053554

(87) International publication number:
WO 2014/042781 (20.03.2014 Gazette 2014/12)

(54) **PROCESS USING HIGH SURFACE AREA ELECTRODES FOR THE ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE**

VERFAHREN UNTER VERWENDUNG VON ELEKTRODEN MIT GROSSEM OBERFLÄCHENBEREICH ZUR ELEKTROCHEMISCHEN REDUKTION VON KOHLENSTOFFDIOXID

PROCÉDÉ UTILISANT DES ÉLECTRODES À SURFACE ÉLEVÉE POUR LA RÉDUCTION ÉLECTROCHIMIQUE DE DIOXYDE DE CARBONE

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(30) Priority: **14.09.2012 US 201261701237 P**
19.09.2012 US 201261703232 P
19.09.2012 US 201261703234 P
19.09.2012 US 201261703231 P
19.09.2012 US 201261703229 P
19.09.2012 US 201261703238 P
19.09.2012 US 201261703175 P
19.09.2012 US 201261703158 P
19.09.2012 US 201261703187 P
31.10.2012 US 201261720670 P
21.12.2012 US 201213724885

(43) Date of publication of application:
22.07.2015 Bulletin 2015/30

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Description

FIELD

[0001] The present disclosure generally relates to the field of electrochemical reactions, and more particularly to methods for electrochemical reduction of carbon dioxide using high surface area electrodes.

BACKGROUND

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

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

[0004] WO2007/041872 A1 describes a continuous co-current electrochemical reduction of carbon dioxide. US 5,290,404 describes an electro-synthesis of alcohols and carboxylic acids from corresponding metal salts. US4,589,963 describes a process for the conversion of salts of carboxylic acid to their corresponding free acids.

SUMMARY OF THE PREFERRED EMBODIMENTS

[0005] The present invention is directed to a method for electrochemical reduction of carbon dioxide into products, comprising:

(A) introducing an acidic anolyte to a first compartment of a first electrochemical cell, the first compartment including an anode;
(B) introducing a catholyte including an alkali metal bicarbonate to a second compartment of the first electrochemical cell, the catholyte saturated with carbon dioxide, the second compartment including a high surface area cathode, the high surface area cathode having a specific surface area of greater than 2 cm^2/cm^3 and including an indium coating and having a void volume of between 30% to 98%, at least a portion of the bicarbonate-based catholyte being recycled;
(C) applying an electrical potential between the anode and the cathode sufficient to reduce the carbon dioxide to an alkali metal formate;
(D) introducing the alkali metal formate to an ion exchange compartment of a second electrochemical cell ;
(E) applying an electrical potential between an anode of the second electrochemical cell and a cathode of the second electrochemical cell sufficient to produce at least formic acid and an alkali metal hydroxide; and
(F) introducing the alkali metal hydroxide with carbon dioxide to generate at least a portion of the alkali metal bicarbonate introduced to the second compartment of the first electrochemical cell.

It is suitably using high surface area electrodes and particular electrolyte solutions to produce single carbon (C1) chemicals, including formic acid, and multi-carbon (C2+) based chemicals (i.e., chemicals with two or more carbon atoms in the compound).

[0006] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not necessarily restrictive of the disclosure as claimed. The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate an embodiment of the disclosure and together with the general description, serve to explain the principles of the disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] The numerous advantages of the present disclosure may be better understood by those skilled in the art by reference to the accompanying figures in which:

FIG. 1 is a flow diagram of a preferred electrolyzer system for the reduction of carbon dioxide in accordance with an embodiment of the present disclosure;
FIG. 2 is a flow diagram of a preferred electrochemical acidification system;

FIG. 3 is a flow diagram of another preferred system for the electrochemical reduction of carbon dioxide;
FIG. 4 is a flow diagram of another preferred electrochemical acidification system incorporating bipolar membranes;
FIG. 5 is flow diagram of another preferred electrochemical electrolyzer system incorporating an ion exchange compartment for the reduction of carbon dioxide; and
FIG. 6 is a flow diagram of a nano-filtration system in accordance with an embodiment of the present disclosure;
FIG. 7 is a chart illustrating cumulative yield of formate over time in accordance with an embodiment described with reference to Example 1 of the present disclosure;
FIG. 8 is a chart illustrating cumulative yield of formate over time in accordance with an embodiment described with reference to Example 2 of the present disclosure;
FIG. 9 is a chart illustrating cumulative yield of formate over time in accordance with an embodiment described with reference to Example 3 of the present disclosure;
FIG. 10 is a chart illustrating cumulative yield of formate over time in accordance with an embodiment described with reference to Example 4 of the present disclosure;
FIG. 11 is a chart illustrating cumulative formate yield versus time in accordance with an embodiment described with reference to Example 9 of the present disclosure;
FIG. 12 is a chart illustrating formate concentration versus time in accordance with an embodiment described with reference to Example 9 of the present disclosure;
FIG. 13 is a chart illustrating cumulative formate yield versus time in accordance with an embodiment described with reference to Example 10 of the present disclosure;
FIG. 14 is a chart illustrating formate concentration versus time in accordance with an embodiment described with reference to Example 10 of the present disclosure;
FIG. 15 is a chart illustrating operating cell voltage versus time in accordance with an embodiment described with reference to Example 11 of the present disclosure;
FIG. 16 is a chart illustrating catholyte formate concentration versus time in accordance with an embodiment described with reference to Example 11 of the present disclosure;
FIG. 17 is a chart illustrating formate current efficiency versus time in accordance with an embodiment described with reference to Example 11 of the present disclosure;
FIG. 18 is a chart illustrating catholyte pH versus time in accordance with an embodiment described with reference to Example 11 of the present disclosure;
FIG. 19 is a chart illustrating formate current efficiency versus time in accordance with an embodiment described with reference to Example 12 of the present disclosure;
FIG. 20 is a chart illustrating catholyte formate concentration versus time in accordance with an embodiment described with reference to Example 12 of the present disclosure; and
FIG. 21 is a chart illustrating catholyte pH versus time in accordance with an embodiment described with reference to Example 12 of the present disclosure.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0008] Reference will now be made in detail to the presently preferred embodiments of the present disclosure, examples of which are illustrated in the accompanying drawings.

[0009] In accordance with some embodiments of the present disclosure, an electrochemical system is provided that converts carbon dioxide to organic products including formate and formic acid. Use of a cathode comprising a high surface area three dimensional material, an acidic anolyte, and a catholyte comprising bicarbonate facilitates the process.

[0010] Before any embodiments of the invention are explained in detail, it is to be understood that the embodiments described below do not limit the scope of the claims that follow. Also, it is to be understood that the phraseology and terminology used herein is for the purpose of description and should not be regarded as limiting. The use of terms such as "including," "comprising," or "having" and variations thereof herein are generally meant to encompass the item listed thereafter and equivalents thereof as well as additional items. Further, unless otherwise noted, technical terms may be used according to conventional usage.

[0011] Referring to FIG. 1, a flow diagram of an electrolyzer system 100 is shown in accordance with an embodiment of the present invention. The electrolyzer system 100 may be utilized for the electrochemical reduction of carbon dioxide to organic products or organic product intermediates. The electrolyzer system 100 reduces carbon dioxide to an alkali metal formate, such as potassium formate. The electrolyzer system 100 generally includes an electrolyzer 102, an anolyte recycle loop 104, and a catholyte recycle loop 106. The electrolyzer system 100 may include as process feeds/inputs carbon dioxide, a catholyte comprising bicarbonate (preferably potassium bicarbonate, but other bicarbonate-based compounds are contemplated instead of or in addition to potassium bicarbonate), and an acidic anolyte (preferably sulfuric acid, but may include other acids, instead of, or in addition to sulfuric acid). The product of the electrolyzer system 100 is generally an alkali metal formate, such as potassium formate, and may include excess catholyte, carbon dioxide,

hydrogen, oxygen, and/or other unreacted process inputs.

[0012] The electrolyzer 102 generally includes an anode compartment 108 and a cathode compartment 110, and may further include a cation exchange membrane 112 to separate the anode compartment 108 from the cathode compartment 110. The anode compartment 108 includes an anode 114 suitable to oxidize water. In a preferred implementation, the anode 114 is a titanium anode having an anode electrocatalyst coating which faces the cation exchange membrane 112. For instance, the anode 114 may include an anode mesh screen 116 that includes a folded expanded titanium screen with an anode electrocatalyst coating. The anode mesh screen 116 may provide spacing and contact pressure between the anode 114 and the cation exchange membrane 112. The anode 114 may also include one or more electrical current connection posts (not shown) on a backside of the anode 114.

[0013] The cathode compartment 110 generally includes a cathode 118 mounted within the cathode compartment 110. The cathode 118 preferably includes a metal electrode with an active electrocatalyst layer on a front surface of the cathode 118 facing the cation exchange membrane 112, and may include one or more electrical current conduction posts (not shown) on a backside of the cathode 118. The cathode 118 includes a high surface area cathode structure 120. The high surface area cathode structure 120 may be mounted between the cation exchange membrane 112 and the cathode 118 for conducting electrical current into the high surface area cathode structure 120. The interface between the high surface area cathode structure 120 and the cation exchange membrane 112 may include an insulator screen (not shown), such as a thin expanded plastic mesh insulator screen to minimize direct contact between the high surface area cathode structure 120 and the cation exchange membrane 112.

[0014] The anode compartment 108 generally includes an anode feed stream 122 that includes a dilute acid anolyte solution. The anode feed stream 122 may enter a bottom of the anode compartment 108 to flow by a face of the anode 114 and through the anode mesh screen 116. The reaction in the anode compartment 108 may include deriving oxygen (O_2, i.e., gaseous oxygen) and hydrogen ions (H^+) or protons from the oxidation of water at an applied current and voltage potential. The hydrogen ions or protons are generally available for the reactions within the cathode compartment 110 via the cation exchange membrane 112. The gaseous oxygen and other liquids leaving the anode compartment 108 of the electrolyzer 102 leave as anode exit stream 124. The anode exit stream 124 may be monitored by a temperature sensor 126a and may flow to an anolyte disengager 128 suitable for separating the oxygen from the anode exit stream 124. The anolyte disengager 128 may process the anode exit stream 124 into an oxygen stream 130, an anolyte recycle stream 132, and an anolyte overflow stream 134. The oxygen stream 130 may be vented from the anolyte disengager 128. The anolyte stream 132 may be combined with water (preferably deionized water) from a water source 136 and with acid (preferably sulfuric acid) from an acid source 138. The water source 136 and the acid source 138 in the anolyte recycle loop 104 may maintain anolyte acid strength and volume for the anode feed stream 122. The temperature of the anode feed stream 122 may be regulated by a heat exchanger 140a coupled with a cooling water source 142a prior to entering the anode compartment 108 of the electrolyzer 102.

[0015] The cathode compartment 110 generally includes a cathode feed stream 144 that includes carbon dioxide and a catholyte. In a preferred implementation, the catholyte is a bicarbonate compound, such as potassium bicarbonate ($KHCO_3$), which is saturated with carbon dioxide. The cathode feed stream 144 may enter a bottom of the cathode compartment 110 to flow by a face of the cathode 118 and through the high surface area cathode structure 120. The reaction in the cathode compartment 110 may reduce carbon dioxide to formate at an applied current and voltage potential. The reaction products and any unreacted materials (e.g., excess catholyte solution) may exit the cathode compartment 110 as cathode exit stream 146. The cathode exit stream 146 may be monitored by a pH sensor 148a and a temperature sensor 126b and may flow to a catholyte disengager 150 suitable for separating gaseous components (e.g., hydrogen) from the cathode exit stream 146. The catholyte disengager 150 may process the cathode exit stream 146 into a hydrogen stream 152, a product stream 154, and a catholyte recycle stream 156. The hydrogen stream 152 may be vented from the catholyte disengager 150. The product stream 154 preferably includes an alkali metal formate (such as potassium formate where the electrolyte includes potassium bicarbonate) and may include excess catholyte. The catholyte stream 156 may be processed by a catholyte recirculation pump 158 and a heat exchanger 140b coupled with a cooling water source 142b. A temperature sensor 126c may monitor the catholyte stream 156 downstream from the heat exchanger 140b having cooling water source 142b. A fresh catholyte electrolyte feed 160 may be metered into the catholyte stream 156, where the fresh catholyte electrolyte feed 160 may adjust the pH of the cathode feed stream 144 into the cathode compartment 110 of the electrolyzer 102, which may control final product overflow rate and establish the formate product concentration. The pH may be monitored by pH sensor 148b. A carbon dioxide stream 162 may be metered into the cathode feed stream 144 downstream from the catholyte electrolyte feed 160 prior to entering the cathode compartment 110 of the electrolyzer 102. The carbon dioxide saturates the catholyte entering the cathode compartment.

[0016] When using an acidic anolyte, where protons are passed through the membrane into the cathode compartment, the pH of the electrolyzer 102 may be controlled or maintained through use of an alkali metal bicarbonate and/or carbonate in combination with water to control the pH of the catholyte. By controlling the pH of the catholyte at an optimum value, the cell may more efficiently convert carbon dioxide into C1 and C2 products with a higher conversion rate than if a non-

optimum pH value was maintained or if no pH control mechanism was employed. In a preferred process, the catholyte is constantly recirculated to maintain an adequate and uniform carbon dioxide concentration at cathode surfaces coated with an electrocatalyst. A fresh catholyte feed stream may be used to control the pH of the catholyte and to control the product concentration in the product overflow stream. The mass flow rate of the catholyte feed to the cathode compartment (e.g., mass flow of potassium bicarbonate) is preferably balanced with the introduction of protons into the catholyte and with the formation of hydroxide from the inefficient byproduct reaction of water splitting at the cathode. The concentration of the potassium bicarbonate is important, since it provides volume to the catholyte, which will dilute the product in the catholyte.

[0017] For pH control of the catholyte, potassium bicarbonate is preferred, in a concentration range of 5 to 600 gm/L, or more preferably in the 10 to 500 gm/L range. If the feed concentration of bicarbonate to the catholyte is fixed, a separate feed of water may be employed into the catholyte to control final product concentration. In another implementation, potassium carbonate may be used as a feed for pH control. Potassium carbonate has a much higher solubility in water than potassium bicarbonate, and is preferably used in a concentration range of 5 to 1,500 gm/L.

[0018] Referring now to FIG. 2, a block diagram of an electrochemical acidification system 200 is shown in accordance with an embodiment of the present invention. The electrochemical acidification system 200 may be utilized to acidify the product stream 154 from the electrolyzer system 100. The electrochemical acidification system 200 acidifies an alkali metal formate, such as potassium formate, to form an organic acid, such as formic acid, and co-produce an alkali metal hydroxide, such as potassium hydroxide. The electrochemical acidification system 200 generally includes an electrochemical acidification unit 202, an anolyte recycle loop 204, and a catholyte recycle loop 206. The electrochemical acidification system 200 may include as process feeds/inputs the product stream 154 from the electrolyzer system 100 (which preferably includes an alkali metal formate), water in each of the anolyte recycle loop 204 and the catholyte recycle loop 206, and an acidic anolyte (preferably sulfuric acid, but may include other acids, instead of, or in addition to sulfuric acid). The product of the electrochemical acidification system 200 is generally an organic acid, such as formic acid, and an alkali metal hydroxide, and may include residual alkali metal formate, bicarbonate catholyte, carbon dioxide, hydrogen, oxygen, and/or other unreacted process inputs.

[0019] The electrochemical acidification unit 202 is preferably a three-compartment electrochemical acidification unit or cell. The electrochemical acidification unit 202 generally includes an anode compartment 208, a cathode compartment 210, and a central ion exchange compartment 212 bounded by cation exchange membranes 214a and 214b on each side. The anode compartment 208 includes an anode 216 suitable to oxidize water. In a preferred implementation, the anode 216 is a titanium anode having an anode electrocatalyst coating which faces the cation exchange membrane 214a. The cathode compartment 210 includes a cathode 218 suitable to reduce water and to generate an alkali metal hydroxide. In a preferred implementation, hydrogen ions (H^+) or protons are generated in the anode compartment 208 when a potential and current are applied to the electrochemical acidification unit 202. The hydrogen ions (H^+) or protons pass through the cation exchange membrane 214a into the central ion exchange compartment 212. The product stream 154 from the electrolyzer system 100 is preferably introduced to the electrochemical acidification unit 202 via the central ion exchange compartment 212, where the hydrogen ions (H^+) or protons displace the alkali metal ions (e.g., potassium ions) in the product stream 154 to acidify the stream and produce a product stream 260 including an organic acid product, preferably formic acid. The displaced alkali metal ions may pass through the cation exchange membrane 214b to the cathode compartment 210 to combine with hydroxide ions (OH^-) formed from water reduction at the cathode 218 to form an alkali metal hydroxide, preferably potassium hydroxide.

[0020] The central ion exchange compartment 212 may include a plastic mesh spacer (not shown) to maintain the dimensional space in the central ion exchange compartment 212 between the cation exchange membranes 214a and 214b. In an embodiment, a cation ion exchange material 220 is included in the central ion exchange compartment 212 between the cation exchange membranes 214a and 214b. The cation ion exchange material 220 may include an ion exchange resin in the form of beads, fibers, and the like. It is contemplated that the cation ion exchange material 220 may increase electrolyte conductivity in the ion exchange compartment solution, and may reduce the potential effects of carbon dioxide gas on the cell voltage as bubbles are formed and pass through the central ion exchange compartment 212.

[0021] The anode compartment 208 generally includes an anode feed stream 222 that includes an acid anolyte solution (preferably a sulfuric acid solution). The gaseous oxygen and other liquids leaving the anode compartment 208 of the electrochemical acidification unit 202 leave as anode exit stream 224. The anode exit stream 224 may be monitored by a temperature sensor 226a and may flow to an anolyte disengager 228 suitable for separating the oxygen from the anode exit stream 224. The anolyte disengager 228 may process the anode exit stream 224 into an oxygen stream 230, an anolyte recycle stream 232, and an anolyte overflow stream 234. The oxygen stream 230 may be vented from the anolyte disengager 228. The anolyte stream 232 may be combined with water (preferably deionized water) from a water source 236 and with acid (preferably sulfuric acid) from an acid source 238. The water source 236 and the acid source 238 in the anolyte recycle loop 204 may maintain anolyte acid strength and volume for the anode feed stream 222. The temperature of the anode feed stream 222 may be regulated by a heat exchanger 240a coupled with a cooling water

source 242a prior to entering the anode compartment 208 of the electrochemical acidification unit 202.

[0022] The cathode compartment 210 generally includes a catholyte feed stream 244 that includes water and may include an alkali metal hydroxide that circulates through the catholyte recycle loop 206. The reaction products, which may include the alkali metal hydroxide and hydrogen gas, may exit the cathode compartment 210 as cathode exit stream 246. The cathode exit stream 246 may be monitored by a temperature sensor 226b and may flow to a catholyte disengager 248 suitable for separating gaseous components (e.g., hydrogen) from the cathode exit stream 246. The catholyte disengager 248 may process the cathode exit stream 246 into a hydrogen stream 250, a catholyte stream 252, and a catholyte overflow stream 254, which may include KOH. The hydrogen stream 250 may be vented from the catholyte disengager 248. The catholyte stream 252 preferably includes an alkali metal hydroxide (such as potassium hydroxide where the product steam 154 includes potassium formate). The catholyte stream 252 may be processed by a catholyte recirculation pump 256 and a heat exchanger 240b coupled with a cooling water source 242b. A temperature sensor 226c may monitor the catholyte stream 252 downstream from the heat exchanger 240b. The catholyte stream 252 may be combined with water (preferably deionized water) from a water source 258, where the water may be metered to control the concentration of the alkali metal hydroxide in the catholyte feed stream 244 entering the cathode compartment 210.

[0023] Referring now to FIG. 3, a flow diagram of a preferred system 300 for the electrochemical reduction of carbon dioxide to an organic acid product is shown. The system 300 may incorporate the electrolyzer system 100 (described with reference to FIG. 1) and the electrochemical acidification system 200 (described with reference to FIG. 2), and preferably includes a potassium hydroxide recycle loop 302 suitable for the production of potassium bicarbonate from potassium hydroxide and carbon dioxide. The system 300 may also incorporate carbon dioxide processing components for the separation (e.g., gas separation units 304a, 304b, 304c, 304d) and recovery of carbon dioxide from process streams.

[0024] The system 300 generally includes carbon dioxide, an alkali metal hydroxide (preferably potassium hydroxide), an acid (preferably sulfuric acid), and water (preferably deionized water) as process inputs and generally includes an organic acid (preferably formic acid), oxygen gas, and hydrogen gas as process outputs. The organic acid may undergo additional processing to provide a desired form and concentration. Such processing may include evaporation, distillation, or another suitable physical separation/concentration process.

[0025] The chemistry of the reduction of carbon dioxide in the system 300 may be as follows.

[0026] Hydrogen atoms are adsorbed at the electrode from the reduction of water as shown in equation (1).

$$H^+ + e^- \rightarrow H_{ad} \qquad (1)$$

[0027] Carbon dioxide is reduced at the cathode surface with the adsorbed hydrogen atom to form formate, which is adsorbed on the surface as in equation (2).

$$CO_2 + H_{ad} \rightarrow HCOO_{ad} \qquad (2)$$

[0028] The adsorbed formate on the surface then reacts with another adsorbed hydrogen atom to form formic acid that is then released into the solution as in equation (3)

$$HCOO_{ad} + H_{ad} \rightarrow HCOOH \qquad (3)$$

[0029] The competing reaction at the cathode is the reduction of water where hydrogen gas is formed as well as hydroxide ions as in equation (4).

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (4)$$

[0030] The anode reaction is the oxidation of water into oxygen and hydrogen ions as shown in equation (5).

$$2H_2O \rightarrow 4H^+ + 4e^- + O_2 \qquad (5)$$

High Surface Area Cathode

[0031] As described with reference to FIG. 1, the cathode 118 includes a high surface area cathode structure 120. The high surface area cathode structure 120 includes a void volume ranging from 30% to 98%. The specific surface area of the high surface area cathode structure 120 is preferably from 2 cm^2/cm^3 to 500 cm^2/cm^3. The surface area also can be defined as total area in comparison to the current distributor/ conductor back plate, with a preferred range of 2x

to 1000x or more.

[0032] The cathode 118 preferably includes electroless indium on tin (Sn) coated copper woven mesh, copper screen, copper fiber as well as bronze and other are copper-tin alloys, nickel and stainless steels. The metals may be precoated with other metals, such as to adequately form a suitable base for the application of the indium and other preferred cathode coatings. The cathode may also include Indium-Cu intermetallics formed on the surfaces of copper fiber, woven mesh, copper foam or copper screen. The intermetallics are generally harder than the soft indium metal, and may provide desirable mechanical properties in addition to usable catalytic properties. The cathode may also include, but is not limited to coatings and/or metal structures containing Pb, Sn, Hg, Tl, In, Bi, and Cd, their alloys, and combinations thereof. Metals including Ti, Nb, Cr, Mo, Ag, Cd, Hg, Tl, An, and Pb as well as Cr-Ni-Mo steel alloys among many others may be incorporated. The cathode 118 may include a single or multi-layered electrode coating, such that the electrocatalyst coating on the cathode substrate includes one or more layers of metals and alloys. A preferred electrocatalyst coating on the cathode includes a tin coating on a high surface area copper substrate with a top layer/coating of indium. The indium coating coverage preferably ranges from 5% to 100% as indium.

[0033] In the use of indium alloys on the exposed catalytic surfaces of the electrode, the indium composition preferably ranges from 5% to 99% as indium in alloys with other metals, including Sn, Pb, Hg, Tl, Bi, Cu, and Cd and their mixed alloys and combinations thereof. It is also contemplated to include Au, Ag, Zn, and Pd into the coating in percentages ranging from 1% to 95%.

[0034] Additionally, metal oxides may be used or prepared as electrocatalysts on the surfaces of the base cathode structure. For example, lead oxide can be prepared as an electrocatalyst on the surfaces of the base cathode structure. The metal oxide coating could be formed by a thermal oxidation method or by electrodeposition followed by chemical or thermal oxidation.

[0035] Additionally, the cathode base structure can also be gradated or graduated, such that the density of the cathode can be varied in the vertical or horizontal directions in terms of density, void volume, or specific surface area (e.g., varying fiber sizes). The cathode structure may also consist of two or more different electrocatalyst compositions that are either mixed or located in separate regions of the cathode structure in the catholyte compartment.

[0036] During normal operation of the electrolyzer 102, the performance of the system may decrease with regard to formate yield which may result from catalyst loss or over-coating of the catalyst with impurities, such as other metals that may be plated onto the cathode 118. The surfaces of the cathode 118 may be renewed by the periodic addition of indium salts or a mix of indium/tin salts *in situ* during operation of the electrolyzer 102. Depending on the composition of the cathode 118, it is contemplated that other or additional metal salts may be added *in situ* including salts of Ag, Au, Mo, Cd, Sn, and other suitable metals, singly or in combination. The electrolyzer 102 may be operated at full rate during operation, or temporarily operated at a lower current density with or without any carbon dioxide addition during the injection of the metal salts. The conditions under which to renew the cathode surface with the addition of these salts may differ depending on desired renewal results. The use of an occasional brief current reversal during electrochemical cell operation may also be employed to potentially renew the cathode surfaces.

[0037] In particular embodiments, the electrolyzer 102 is operated at pressures exceeding atmospheric pressure, which may result in higher current efficiency and permit operation of the electrolyzer 102 at higher current densities than when operating the electrolyzer 102 at or below atmospheric pressure.

[0038] In preparing cathode materials for the production of organic chemicals, the addition of metal salts that can reduce on the surfaces of the cathode structure can be also used, such as the addition of Ag, Au, Mo, Cd, Sn, and other suitable metals. Such addition of metal salts may provide a catalytic surface that may be otherwise difficult to prepare directly during cathode fabrication or for renewal of the catalytic surfaces.

[0039] A preferred method for preparing the high surface area cathode structure 120 is using an electroless plating solution which may include an indium salt, at least one complexing agent, a reducing agent, a pH modifier, and a surfactant. The preferred procedure for forming an electroless indium coating on the high surface area cathode may include combining in stirred deionized water the following materials: Trisodium citrate dihydrate (100g/L), EDTA-disodium salt (15g/L), sodium acetate (10g/L), $InCl_3$ (anhydrous, 10g/L), and Thiodiglycolic acid (0.3g/L, e.g., 3 mL of 100mg/mL solution). A pre-mixed stock deposition solution that has been stirred (preferably for multiple hours, e.g., overnight) may also be used. The procedure also includes heating the mixture to about 40°C. The procedure also includes adding 40 mL $TiCl_3$ (20 wt. % in 2% HCl) per liter [0.05 mM] and adding 7M ammonia in methanol until the pH of the mixture is approximately 7 (-15 mL ammonia solution per liter) at which point ammonium hydroxide (28% ammonia solution) is used to adjust the pH to between approximately 9.0 and 9.2. The procedure then includes heating the mixture to about 60°C. If the pH drops, adjust the pH to approximately 9.0 with ammonium hydroxide solution. The procedure then includes heating the mixture to about 75°C, where deposition may begin at about 65°C. The procedure includes holding the mixture at 75°C for about one hour.

[0040] A preferred procedure for the metallic coating of copper substrates may include rinsing bare copper substrates in acetone to clean the copper surface (e.g., removing residual oils or grease that may be present on the copper surface) and then rinsing the acetone-treated copper substrates in deionized water. The procedure also includes immersing the

bare copper substrates in a 10% sulfuric acid bath for approximately 5 minutes, and then rinsing with deionized water. The procedure also includes depositing approximately 25 μm of tin on the copper surface. The deposition may be done using a commercial electroless tinning bath (Caswell, Inc.) operated at 60 °C for 15 minutes. Following tin deposition, parts are rinsed thoroughly in deionized water. The procedure also includes depositing approximately 1 μm of indium on the tinned copper surface. The deposition may be done using an electroless bath operated at 90 °C for 60 minutes. Following indium deposition, parts are rinsed thoroughly in deionized water. The procedure may also include treated the copper/tin/indium electrode in a 5 wt% nitric acid bath for 5 minutes. Such treatment may improve electrode stability as compared to an untreated copper/tin/indium electrode. In another implementation, the electroless tin plated copper substrate may be dipped into molten indium for coating.

[0041] In particular implementations, cathode substrates may be treated with catalytic materials for carbon dioxide reduction. Four example treatments are presented by the following.

[0042] A first treatment may include coating a conductive substrate (e.g., vitreous carbon or metal) in a conductive sol-gel containing sufficient catalyst material to yield a high active surface area. The conductive component of the sol-gel may be catalytically active. After coating the substrate with the catalytic sol-gel, the sol-gel is allowed to undergo a high degree of polymerization/cross-linking. The combined substrate/sol-gel structure may then be pyrolized at high temperature to convert organic material to amorphous (and potentially conductive) carbon. The pyrolized structure may also be subjected to chemical treatments that selectively remove the organic material or the silica phase, leading to a high catalyst content coating.

[0043] The second treatment may include binding relatively small particles (e.g., micron or nanometer scale) to a substrate using a binding agent such as amines, thiols, or other suitable binding agent. The binding agent is preferably conductive to pass current between the substrate and catalyst particles. The catalyst particles preferably include conjugated organic molecules, such as diphenybenzene. If the substrate is also made of catalyst material the binding agent may have symmetrical binding groups, otherwise binding agents with two different binding groups may be utilized.

[0044] The third treatment may include coating a substrate in a slurry containing catalyst material (which may be in salt form) and a binding agent. The slurry may also contain a conductive additive, such as carbon black, carbon nanotubes, or other suitable conductive additive. The slurry coating may then be dried to form a conformal coating over the substrate. The substrate and dried slurry coating may be heated in order to fuse the various constituent materials into a mechanically robust, conductive, and catalytic material. In a particular implementation, the heating of the substrate and dried slurry coating occurs in a reducing environment.

[0045] The fourth treatment may include coating a substrate with semiconducting metal chalcogenides by applying a precursor to the substrate, removing solvent, and baking the substrate to convert the precursor material to a monolithic semiconducting metal chalcogenide coating. The coating materials may include, but are not limited to, Na_4SnS_4, $Na_4Sn_2S_6$, K_4SnTe_4, Na_3AsS_3, $(NH_4)_4Sn_2S_6$, $(NH_4)_3AsS_3$, and $(NH_4)_2MoS_4$.

[0046] Other coating and electrocatalyst preparation techniques include applying thermal oxides onto a substrate, forming an intermetallic with a substrate, and applying semiconductor materials on a substrate. In an embodiment, the thermal oxidation of various metal salts painted onto various metal and ceramic substrates is preferred for forming high surface area materials suitable for the electrochemical reduction of carbon dioxide. The thermal oxidation may be similar to that used for forming electrocatalysts on titanium for use as anode materials in electrochemical chlorine cells, such as iridium oxide and ruthenium oxide. In another embodiment, indium is electroplated onto a copper foil, then the copper foil is heated to 40°C above the melting point of indium, until indium is melted on the foil surface, and forming a golden intermetallic with copper, and then cooled. The formation of the intermetallic can be done in air or under an inert gas atmosphere (e.g., argon or helium) or under a full or partial vacuum. The electroplated material preferably provides approximately 50% Faradaic conversion efficiency, and may be utilized as a coating on planar metal back plates and also on copper fibers. An intermetallic may also be formed with tin-plated copper substrates. In a further embodiment, a semiconductor material may be applied to a substrate by gaseous deposition, sputtering, or other suitable application methods. The substrate is preferably a metallic substrate. The semiconductor materials may be doped to P-type or N-type as desired.

[0047] In the four treatments and other coating techniques described above, certain measures may be taken to improve the quality (mechanical, electrical, etc.) of the bond between the substrate and catalyst. Such measures may involve creating functional groups on the substrate surface that can undergo chemical bonding with the catalyst or a binding agent, or the creation of geometrical features in the substrate surface that facilitate bonding with an applied catalyst coating.

[0048] The substrate for the high surface area cathodes described herein may include RVC materials, such as carbon and graphite, metal foams, woven metals, metal wools made from fibers, sintered powder metal films and plates, metal and ceramic beads, pellets, ceramic and metal column and trickle bed packing materials, metal and inorganic powder forms, metal fibers and wools, or other suitable substrate materials. The specific surface area of the physical forms preferably include a specific surface area between approximately 2 and 2,000 cm^2/cm^3 or greater.

[0049] The electrode or high surface area structure of an electrode may incorporate alloys as fibers or wools, and may

be coated with various compounds, and subsequently fired in air or in a reducing atmosphere oven, to form stable oxides on the surfaces which are electrocatalytic in the reduction of carbon dioxide. Other cathode materials may include metallic glasses and amorphous metals.

[0050] Referring now to FIG. 4, a particular implementation of the acid acidification system 200 of FIG. 2 is shown utilizing bipolar membranes in an electrochemical acidification unit 402. By utilizing bipolar membranes in electrochemical acidification unit 402, the alkali metal formate (e.g., potassium formate) may be acidified in addition to recovering potassium hydroxide. The use of the bipolar membranes may reduce the voltage required for the acidification of the alkali metal formate and may reduce the number of actual anodes and cathodes needed for the electrochemical stack. The bipolar membranes preferably consist of a cation membrane and an anion membrane that have been bonded together, and function by splitting water at the two membrane interface, forming hydrogen (H^+) ions from the cation membrane and hydroxide ions (OH^-) from the anion membrane.

[0051] Referring now to FIG. 5, an alternative embodiment of the electrochemical system 100 of FIG. 1 is shown. The electrolyzer 502 in FIG. 5 includes an ion exchange compartment 504 in addition to an anode 506 compartment and a cathode compartment 508. This ion exchange compartment 504 functions similarly as the acid acidification compartment 212 in electrochemical acidification unit 202 as shown in FIG. 2. The alkali metal formate product (e.g., potassium formate) and unreacted $KHCO_3$ from the cathode compartment is passed through the ion exchange compartment 504 to provide a formic acid product with CO_2 and some residual $KHCO_3$. The hydrogen ions (H^+) passing through the adjacent membrane 510a on the anode compartment side displace the alkali metal ions (e.g., K^+) in the stream passing through the central ion exchange compartment 504 so that the alkali metal formate is acidified and the alkali metal ions and remaining hydrogen ions pass through the adjoining membrane 510b on the cathode compartment 508 and into the catholyte. This will allow operation of the catholyte at higher pH conditions if required for obtaining high Faradaic current efficiencies with the cathodes selected for the process.

[0052] In an indium-based cathode system, the preferred catholytes include alkali metal bicarbonates, carbonates, sulfates, phosphates, and the like. Other preferred catholytes include borates, ammonium, and hydroxides. Other catholytes may include chlorides, bromides, and other organic and inorganic salts. Non-aqueous electrolytes, such as propylene carbonate, methanesulfonic acid, methanol, and other ionic conducting liquids may be used, which may be in an aqueous mixture, or as a non-aqueous mixture in the catholyte. The introduction of micro bubbles of carbon dioxide into the catholyte stream may improve carbon dioxide transfer to the cathode surfaces.

[0053] Referring now to FIG. 6, a nano-filtration system may be utilized between the electrolyzer system 100, as shown in FIG. 1, and the electrochemical acidification system 200, as shown in FIG. 2. The nano-filtration system is preferably utilized to separate alkali metal formate (e.g., potassium formate) from bicarbonate leaving the electrolyzer system 100 (e.g., stream 154) to reduce the amount of bicarbonate entering the electrochemical acidification unit 202. The nano-filtration system preferably uses a nano-filtration filter/membrane under pressure for selective separation of the bicarbonate from the alkali metal formate. The nano-filtration filter/membrane separates monovalent anions (e.g., formate) from divalent anions (e.g., carbonate) using a high pressure pump and suitable selected membranes for the separation. When utilizing the nano-filtration system as a separation tool between the electrolyzer system 100 and the electrochemical acidification system 200, the bicarbonate in the formate/bicarbonate product (e.g., stream 154) is preferably converted to carbonate in order to efficiently separate the formate from the carbonate with the nano-filtration filter/membrane. The nano-filtration system may include a mixer, such as a mixing tank, to mix the formate/bicarbonate product stream with a potassium hydroxide (KOH) stream. The mixer may promote the conversion of potassium bicarbonate to potassium carbonate to facilitate the separation of the formate from the carbonate. A high pressure pump then sends the potassium formate/carbonate stream into a nano-filtration unit which includes the nano-filtration filter/membrane. The nano-filtration unit produces a low-carbonate-containing potassium formate permeate stream which is then sent to the electrochemical acidification system 200 as shown in FIG. 2 as stream 154, to enter the electrochemical acidification unit 202. The potassium carbonate containing reject stream leaving the nano-filtration unit is preferably sent to the $KHCO_3$ block of FIG. 3, where the potassium carbonate is mixed with KOH and CO_2 for conversion to potassium bicarbonate. The potassium bicarbonate is preferably utilized as a feed to the cathode compartment of the electrolyzer 102 of the electrolyzer system 100. The nano-filtration separation system may consist of multiple units connected in a series flow configuration to increase the total separation efficiency of the carbonate from formate separation. The system may also utilize recycle streams to recycle an output stream from one unit to the input of another unit to maintain flow and pressures as well as to increase the recovery of the formate.

[0054] Depending on the chemistry of the electrochemical systems described herein, the pH of the catholyte preferably ranges from 3 to 12. The desired pH of the catholyte may be a function of the catholyte operating conditions and the catalysts used in the cathode compartment, such that there is limited or no corrosion at the electrochemical cell.

[0055] Preferable catholyte cross sectional area flow rates may include a range of 2 to 3,000 gpm/ft^2 or more (0.0076 to 11.36 m^3/m^2), with a flow velocity range of 0.002 to 20 ft/sec (0.0006 to 6.1 m/sec).

[0056] A homogenous heterocyclic catalyst is preferably utilized in the catholyte. The homogenous heterocyclic catalyst may include, for example, one or more of 4-hydroxy pyridine, adenine, a heterocyclic amine containing sulfur, a hete-

rocyclic amine containing oxygen, an azole, a benzimidazole, a bipyridine, furan, an imidazole, an imidazole related species with at least one five-member ring, an indole, a lutidine, methylimidazole, an oxazole, phenanthroline, pterin, pteridine, a pyridine, a pyridine related species with at least one six-member ring, pyrrole, quinoline, or a thiazole, and mixtures thereof.

[0057] Preferred anolytes for the system include alkali metal hydroxides, such as KOH, NaOH, LiOH; ammonium hydroxide; inorganic acids such as sulfuric, phosphoric, and the like; organic acids such as methanesulfonic acid; non-aqueous and aqueous solutions; alkali halide salts, such as the chlorides, bromides, and iodine types such as NaCl, NaBr, LiBr, and NaI; and acid halides such as HCl, HBr and HI. The acid halides and alkali halide salts will produce for example chlorine, bromine, or iodine as a halide gas or as dissolved aqueous products from the anolyte compartment. Methanol or other hydrocarbon non-aqueous liquids can also be used, and would form some oxidized organic products from the anolyte. Selection of the anolyte would be determined by the process chemistry product and requirements for lowering the overall operating cell voltage. For example, the formation of bromine at the anode requires a significantly lower anode voltage potential than chlorine formation, and iodine is even lower than that of bromine. This allows for a significant power cost savings in the operation of both of the electrochemical units when bromine is generated in the anolyte. The formation of a halogen, such as bromine, in the anolyte may then be used in an external reaction to produce other compounds, such as reactions with alkanes to form bromoethane, which may then be converted to an alcohol, such as ethanol, or an alkene, such as ethylene, and the halogen acid byproduct from the reaction can be recycled back to the electrochemical cell anolyte.

[0058] Operation of the electrolyzer catholyte at a higher operating pressure may allow more carbon dioxide to dissolve in the aqueous electrolyte than at lower pressures (e.g., ambient pressures). Electrochemical cells may operate at pressures up to about 20 to 30 psig in multi-cell stack designs, although with modifications, they could operate at up to 100 psig. The electrolyzer anolyte may also be operated in the same pressure range to minimize the pressure differential on the membrane separating the two electrode compartments. Special electrochemical designs are required to operate electrochemical units at higher operating pressures up to about 60 to 100 atmospheres or greater, which is in the liquid CO_2 and supercritical CO_2 operating range.

[0059] In a particular implementation, a portion of the catholyte recycle stream may be separately pressurized using a flow restriction with backpressure or using a pump, with CO_2 injection, such that the pressurized stream is then injected into the catholyte compartment of the electrolyzer. Such a configuration may increase the amount of dissolved CO_2 in the aqueous solution to improve the conversion yield.

[0060] Catholyte and anolyte operating temperatures preferably range from -10 to 95 °C, more preferably 5 to 60°C. The minimum operating temperature will be limited to the electrolytes used and their freezing points. In general, the lower the temperature, the higher the solubility of CO_2 in the aqueous solution phase of the electrolyte, and would help in obtaining higher conversion and current efficiencies. A consideration for lower operating temperatures is that the operating electrolyzer cell voltages may be higher, so an optimization may be required to produce the chemicals at the lowest operating cost.

[0061] The electrochemical cell design may include a zero gap, flow-through design with a recirculating catholyte electrolyte with various high surface area cathode materials. Other designs include: flooded co-current packed and trickle bed designs with the various high surface area cathode materials, bipolar stack cell designs, and high pressure cell designs.

[0062] Anodes for use in the electrochemical system may depend on various system conditions. For acidic anolytes and to oxidize water to generate oxygen and hydrogen ions, the anode may include a coating, with preferred electro-catalytic coatings including precious metal oxides, such as ruthenium and iridium oxides, as well as platinum, rhodium, and gold and their combinations as metals and oxides deposited on valve metal substrates, such as titanium, tantalum, zirconium, and niobium. For other anolytes, such as alkaline or hydroxide electrolytes, the anode made include carbon, cobalt oxides, stainless steels, nickel, and their alloys and combinations which may be stable as anodes suitable under alkaline conditions.

[0063] As described herein, the electrochemical system may employ a membrane positioned between the anode compartment and the cathode compartment. Cation ion exchange type membranes are preferred, especially those that have a high rejection efficiency to anions, for example perfluorinated sulfonic acid based ion exchange membranes such as DuPont Nafion® brand unreinforced types N117 and N120 series, more preferred PTFE fiber reinforced N324 and N424 types, and similar related membranes manufactured by Japanese companies under the supplier trade names such as Flemion®. Other multi-layer perfluorinated ion exchange membranes used in the chlor alkali industry have 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. These membranes have a much higher anion rejection efficiency. These are 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. Hydrocarbon based membranes, which are made from various cation ion exchange materials can also be used if the anion rejection is not as critical, such as those sold by Sybron under their trade name Ionac®, AGC Engineering (Asahi

Glass) under their Selemion® trade name, and Tokuyama Soda, among others available on the market.

Example Electrolyzer Design

[0064] The electrolyzer design used in laboratory examples may incorporate various thickness high surface area cathode structures using added spacer frames and also provide the physical contact pressure for the electrical contact to the cathode current conductor backplate.

[0065] An electrochemical bench scale cell with an electrode projected area of about 108 cm^2 was used for much of the bench scale test examples. The electrochemical cell was constructed consisting of two electrode compartments machined from 1.0 inch (2.54 cm) thick natural polypropylene. The outside dimensions of the anode and cathode compartments were 8 inches (20.32 cm) by 5 inches (12.70 cm) with an internal machined recess of 0.375 inches (0.9525 cm) deep and 3.0 inches (7.62 cm) wide by 6 inches (15.24 cm) tall with a flat gasket sealing area face being 1.0 inches (2.52 cm) wide. Two holes were drilled equispaced in the recess area to accept two electrode conductor posts that pass though the compartment thickness, and having two 0.25 inch (0.635 cm) drilled and tapped holes to accept a plastic fitting that passes through 0.25 inch (0.635 cm) conductor posts and seals around it to not allow liquids from the electrode compartment to escape to the outside. The electrode frames were drilled with an upper and lower flow distribution hole with 0.25 inch pipe threaded holes with plastic fittings installed to the outside of the cell frames at the top and bottom of the cells to provide flow into and out of the cell frame, and twelve 0.125 inch (0.3175 cm) holes were drilled through a 45 degree bevel at the edge of the recess area to the upper and lower flow distribution holes to provide an equal flow distribution across the surface of the flat electrodes and through the thickness of the high surface area electrodes of the compartments.

[0066] For the anode compartment cell frames, an anode with a thickness of 0.060 inch (0.1524 cm) and 2.875 inch (7.3025 cm) width and 5.875 inch (14.9225 cm) length with two 0.25 inch (0.635 cm) titanium diameter conductor posts welded on the backside were fitted through the two holes drilled in the electrode compartment recess area. The positioning depth of the anode in the recess depth was adjusted by adding plastic spacers behind the anode, and the edges of the anode to the cell frame recess were sealed using a medical grade epoxy. The electrocatalyst coating on the anode was a Water Star WS-32, an iridium oxide based coating on a 0.060 inch (0.1524 cm) thick titanium substrate, suitable for oxygen evolution in acids. In addition, the anode compartment also employed an anode folded screen (folded three times) that was placed between the anode and the membrane, which was a 0.010 inch (0.0254 cm) thick titanium expanded metal material from DeNora North America (EC626), with an iridium oxide based oxygen evolution coating, and used to provide a zero gap anode configuration (anode in contact with membrane), and to provide pressure against the membrane from the anode side which also had contact pressure from the cathode side.

[0067] For the cathode compartment cell frames, 316L stainless steel cathodes with a thickness of 0.080 inch (0.2032 cm) and 2.875 inch (7.3025 cm) width and 5.875 inch (14.9225 cm) length with two 0.25 inch (0.635 cm) diameter 316L SS conductor posts welded on the backside were fitted through the two holes drilled in the electrode compartment recess area. The positioning depth of the cathode in the recess depth was adjusted by adding plastic spacers behind the cathode, and the edges of the cathode to the cell frame recess were sealed using a fast cure medical grade epoxy.

[0068] A copper bar was connected between the two anode posts and the cathode posts to distribute the current to the electrode back plate. The cell was assembled and compressed using 0.25 inch (0.635 cm) bolts and nuts with a compression force of about 60 in-lbs force. Neoprene elastomer gaskets (0.0625 inch (0.159 cm) thick) were used as the sealing gaskets between the cell frames, frame spacers, and the membranes.

EXAMPLE 1

[0069] The above cell was assembled with a 0.010 inch (0.0254 cm) thickness indium foil mounted on the 316L SS back conductor plate using a conductive silver epoxy. A multi-layered high surface area cathode, comprising an electrolessly applied indium layer of about 1 micron thickness that was deposited on a previously applied layer of electroless tin with a thickness of about 25 micron thickness onto a woven copper fiber substrate. The base copper fiber structure was a copper woven mesh obtained from an on-line internet supplier, PestMall.com (Anteater Pest Control Inc.). The copper fiber dimensions in the woven mesh had a thickness of 0.0025 inches (0.00635 cm) and width of 0.010 inches (0.0254 cm). The prepared high surface area cathode material was folded into a pad that was 1.25 inches (3.175 cm) thick and 6 inches (15.24 cm) high and 3 inches (7.62 cm) wide, which filled the cathode compartment dimensions and exceeded the adjusted compartment thickness (adding spacer) which was 0.875 inches (2.225 cm) by about 0.25 inches (0.635 cm). The prepared cathode had a calculated surface area of about 3,171 cm^2, for an area about 31 times the flat cathode plate area, with a 91% void volume, and specific surface area of 12.3 cm^2/cm^3. The cathode pad was compressible, and provided the spring force to make contact with the cathode plate and the membrane. Two layers of a very thin (0.002 inches thick) plastic screen with large 0.125 inch (0.3175 cm) holes were installed between the cathode mesh and the Nafion® 324 membrane. Neoprene gaskets (0.0625 inch (0.159 cm) thick) were used as the sealing gaskets

between the cell frames and the membranes. The electrocatalyst coating on the anode in the anolyte compartment was a Water Star WS-32, an iridium oxide based coating, suitable for oxygen evolution in acids. In addition, the anode compartment also employed a three-folded screen that was placed between the anode and the membrane, which was a 0.010 inch (0.0254 cm) thick titanium expanded metal material from DeNora North America (EC626), with an iridium oxide based oxygen evolution coating, and used to provide a zero gap anode configuration (anode in contact with membrane), and to provide pressure against the membrane from the anode side which also had contact pressure from the cathode side.

[0070] The cell assembly was tightened down with stainless steel bolts, and mounted into the cell station, which has the same configuration as shown in FIG. 1 with a catholyte disengager, a centrifugal catholyte circulation pump, inlet cell pH and outlet cell pH sensors, a temperature sensor on the outlet solution stream. A 5 micron stainless steel frit filter was used to sparge carbon dioxide into the solution into the catholyte disengager volume to provide dissolved carbon dioxide into the recirculation stream back to the catholyte cell inlet.

[0071] The anolyte used was a dilute 5% by volume sulfuric acid solution, made from reagent grade 98% sulfuric acid and deionized water.

[0072] In this test run, the system was operated with a catholyte composition containing 0.4 molar potassium sulfate aqueous with 2 gm/L of potassium bicarbonate added, which was sparged with carbon dioxide to an ending pH of 6.60.

Operating Conditions:

Batch Catholyte Recirculation Run

[0073]

Anolyte Solution: 0.92 M H_2SO_4
Catholyte Solution: 0.4 M K_2SO_4, 0.14mM $KHCO_3$
Catholyte flow rate: 2.5 LPM
Catholyte flow velocity: 0.08 ft/sec
Applied cell current: 6 amps (6,000 mA)
Catholyte pH range: 5.5 - 6.6, controlled by periodic additions of potassium bicarbonate to the catholyte solution recirculation loop. Catholyte pH declines with time, and is controlled by the addition of potassium bicarbonate.

Results:

[0074]

Cell voltage range: 3.39 - 3.55 volts (slightly lower voltage when the catholyte pH drops)
Run time: 6 hours
Formate Faradaic yield: Steady between 32 - 35%, calculated taking samples periodically. See FIG. 7.
Final formate concentration: 9,845 ppm

EXAMPLE 2

[0075] The same cell as in Example 1 was used with the same cathode, which was only rinsed with water while in the electrochemical cell after the run was completed and then used for this run.

[0076] In this test run, the system was operated with a catholyte composition containing 0.375 molar potassium sulfate aqueous with 40 gm/L of potassium bicarbonate added, which was sparged with carbon dioxide to an ending pH of 7.05.

Operating Conditions:

Batch Catholyte Recirculation Run

[0077]

Anolyte Solution: 0.92 M H_2SO_4
Catholyte Solution: 0.4 M K_2SO_4, 0.4 M $KHCO_3$
Catholyte flow rate: 2.5 LPM
Catholyte flow velocity: 0.08 ft/sec
Applied cell current: 6 amps (6,000 mA)

Catholyte pH range: Dropping from 7.5 to 6.75 linearly with time during the run.

Results:

[0078]

Cell voltage range: 3.40 - 3.45 volts
Run time: 5.5 hours
Formate Faradaic yield: Steady at 52% and slowly declining with time to 44% as the catholyte pH dropped. See FIG. 8.
Final formate concentration: 13,078 ppm

EXAMPLE 3

[0079] The same cell as in Examples 1 and 2 was used with the same cathode, which was only rinsed with water while in the electrochemical cell after the run was completed and then used for this run.

[0080] In this test run, the system was operated with a catholyte composition containing 0.200 molar potassium sulfate aqueous with 40 gm/L of potassium bicarbonate added, which was sparged with carbon dioxide to an ending pH of 7.10.

Operating Conditions:

Batch Catholyte Recirculation Run

[0081]

Anolyte Solution: 0.92 M H_2SO_4
Catholyte Solution: 0.2 M K_2SO_4, 0.4 M $KHCO_3$
Catholyte flow rate: 2.5 LPM
Catholyte flow velocity: 0.08 ft/sec
Applied cell current: 9 amps (9,000 mA)
Catholyte pH range: Dropping from 7.5 to 6.65 linearly with time during the run, and then additional solid $KHCO_3$ was added to the catholyte loop in 10 gm increments at the 210, 252, and 290 minute time marks which brought the pH back up to about a pH of 7 for the last part of the run.

Results:

[0082]

Cell voltage range: 3.98 - 3.80 volts
Run time: 6.2 hours
Formate Faradaic yield: 75% declining to 60% at a pH of 6.65, and then increasing to 75% upon the addition of solid potassium bicarbonate to the catholyte to the catholyte loop in 10 gm increments at the 210, 252, and 290 minute time marks and slowly declining down with time 68% as the catholyte pH dropped to 6.90. See FIG. 9.
Final formate concentration: 31,809 ppm.

EXAMPLE 4

[0083] The same cell as in Examples 1, 2, and 3 was used with the same cathode, which was only rinsed with water while in the electrochemical cell after the run was completed and then used for this run.

[0084] In this test run, the system was operated with a catholyte composition containing 1.40 molar potassium bicarbonate (120 gm/L $KHCO_3$), which was sparged with carbon dioxide to an ending pH of 7.8.

Operating Conditions:

Batch Catholyte Recirculation Run

[0085]

Anolyte Solution: 0.92 M H_2SO_4

Catholyte Solution: 1.4 M $KHCO_3$
Catholyte flow rate: 2.6 LPM
Catholyte flow velocity: 0.09 ft/sec
Applied cell current: 11 amps (11,000 mA)
Catholyte pH range: Dropping from around 7.8 linearly with time during the run to a final pH of 7.48

Results:

[0086]

Cell voltage range: 3.98 - 3.82 volts
Run time: 6 hours
Formate Faradaic yield: 63% and settling down to about 54 - 55%. See FIG. 10.
Final formate concentration: 29,987 ppm.

Prophetic EXAMPLE 5

[0087] This example contemplates separation of product potassium formate from potassium carbonate/bicarbonate supporting electrolyte by membrane nano-filtration (NF) (FIG. 10). The test would involve two commercial NF membranes. The feed solution would comprise 1.2M $KHCO_3$ + 0.6M K-formate and its pH would be adjusted to 7, 9, and 11 for three separate runs (for each membrane).

[0088] All NF tests would be performed in GE-Osmonic Sepa permeator (active membrane area of 0.0137 m^2) at applied pressure of 40 bar (580 psig) and 50°C. During each run 3 liters of feed solution would be passed through and the permeate would be collected into a measuring cylinder (to determine volume) and the elapsed time recorded. The permeate would later be analyzed for total carbonate (HCO_3^- + CO_3^{2-}) and formate. From such data, the permeability (in L/m^2 h bar) and solute rejections (in %) would be calculated as follows:

$$\text{Permeability} = \frac{volume\ collected\ (L)}{membrane\ area(m2)\ x\ \ elapsed\ time(h)}$$

$$\%\ \text{Rejection} = \frac{[S]Feed - [S]Permeate}{[S]Feed} \text{ x } 100$$

Where [S] denotes molar concentration of solute that could be either formate or total carbonate.

Expected results are summarized below:

[0089]

GE-Desal DK membrane

Feed pH	%Rejection		Permeabiility L/m^2 h bar
	Total carbonate	Formate	
7	11.4	2.2	1.72
9	30.3	-9.7	1.07
11	81.8	-46.3	0.36

Dow-Filmtec NF270 membrane

Feed pH	%Rejection		Permeabiility L/m^2 h bar
	Total carbonate	Formate	
7	11.0	2.6	1.91

(continued)

Feed pH	%Rejection		Permeabiility L/m^2 h bar
	Total carbonate	Formate	
9	29.5	-5.4	1.20
11	80.1	-43.8	0.44

Prophetic EXAMPLE 6

[0090] A single permeation test could be performed with DK membrane, using a formate-enriched Feed solution comprising 1.2M $KHCO_3$ + 1.2M K-formate. The test could be done at pH 11 and all other conditions would be as in the above Example 1.

[0091] Such a test would likely give 79.9% and -33.8% rejection for total carbonate and formate, respectively. The permeability would be 0.32 L/m^2 h bar.

EXAMPLE 7

[0092] The same cell as in Examples 1, 2, and 3 was used, except for using 701 gm of tin shot (0.3 - 0.6 mm diameter) media with an electroless plated indium coating as the cathode. The cathode compartment thickness was 0.875 inches.

[0093] In this test run, the system was operated with a catholyte composition containing 1.40 molar potassium bicarbonate (120 gm/L $KHCO_3$), which was sparged with carbon dioxide to an ending pH of 8.0

[0094] The cell was operated in a batch condition with no overflow for the first 7.3 hrs, and then a 1.40 molar potassium bicarbonate feed was introduced into the catholyte at a rate of about 1.4 mL/min, with the overflow collected and measured, and a sample of the loop was collected for formate concentration analysis.

Operating Conditions:

Batch Catholyte Recirculation Run

[0095]

Anolyte Solution: 0.92 M H_2SO_4
Catholyte Solution: 1.4 M $KHCO_3$
Catholyte flow rate: 3.2 LPM
Applied cell current: 6 amps (6,000 mA)
Catholyte pH range: Dropping slowly from around a pH of 8 linearly with time during the run to a final pH of 7.50

Results:

[0096]

Cell voltage range: 3.98 - 3.82 volts
Run time: Batch mode: 7.3 hours
Feed and product overflow: 7.3 hours to end of run at 47 hours.

[0097] The formate Faradaic efficiency was between 42% and 52% during the batch run period where the formate concentration went up to 10,490 ppm. During the feed and overflow period, the periodic calculated efficiencies varied between 32% and 49%. The average conversion efficiency was about 44%. The formate concentration varied between 10,490 and 48,000 ppm during the feed and overflow period. The cell voltage began at around 4.05 volts, ending up at 3.80 volts.

EXAMPLE 8

[0098] Electrolyses were performed using a 3-compartment glass cell of roughly 80 mL total volume. The cell was constructed to be gas tight with Teflon bushings. The compartments were separated by 2 glass frits. A 3-electrode assembly was employed. One compartment housed the working electrode and the reference electrode (Accumet sil-

ver/silver chloride) which contained the aqueous electrolyte and catalyst as stated. The center compartment also contained the electrolyte and catalyst solution as stated. The third compartment was filled with 0.5 molar K_2SO_4 aqueous electrolyte solution sparged with CO_2 with a pH of about 4.5 and housed the counter electrode (TELPRO (Stafford, TX) - Mixed Metal Oxide Electrode). The working electrode compartment was purged with carbon dioxide during the experiment. The solutions were measured by ion chromatography for formic acid, analyzing the solution before (a blank) and after electrolysis. The tests were conducted under potentiometric conditions using a 6 channel Arbin Instruments MSTAT, operating at -1.46 or -1.90 volts vs. an SCE reference electrode for about 1.5 hrs.

Cathode Evaluated	Experiment Designation	Formate Produced (ppm)	Formate Yield %	Applied Potential (volts)	Current (ma)	Time (hrs)
Electroplated indium on tin foil	DK80	1,818	75.8	-1.9	50	1.5
Electroplated indium on tin foil	DK82	1,956	64.0	-1.9	58.5	1.5
Untreated tin foil *	DK80	1,260	54.3	-1.9	44.5	1.5
Electroplated indium on copper foil	DK83	1,887	31.7	-1.9	123	1.5
Tin foil (untreated) *	DK80	604	18.0	-1.9	54.8	1.5
Copper screen with electroless indium coating	DK79	1,813	30.6	-1.46	97.9	1.5
Copper screen with electroless indium annealed at 200°C	DK78	1,387	43.9	-1.46	63.6	1.5
* In the above table, entries 3 and 5 are reference examples						

EXAMPLE 9 (reference example)

[0099] The same cell as in Examples 1, 2, and 3 was used, except for using 890.5 gm of tin shot (3 mm diameter) media and with a tin foil coating as the cathode. The cathode compartment thickness was 1.25 inches and the system was operated in a batch mode with no feed input. Carbon dioxide was sparged to saturate the solution in the catholyte disengager.

Packed Tin Bed Cathode Detail:

[0100]

Weight: 890.5 gm tin shot
Tin shot: 3 mm average size
Total compartment volume: 369 cm^3
Calculated tin bead surface area: 4,498 cm^2
Calculated packed bed cathode specific surface area: 12.2 cm^2/cm^3
Calculated packed bed void volume: 34.6%

[0101] In this test run, the system was operated with a catholyte composition containing 1.40 molar potassium bicarbonate (120 gm/L $KHCO_3$), which was sparged with CO_2 to an ending pH of about 8.0

[0102] The cell was operated in a batch condition with no overflow and a sample of the catholyte loop was collected for formate concentration analysis periodically.

Operating Conditions:

[0103]

Batch Catholyte Recirculation Run
Anolyte Solution: 0.92 M H_2SO_4
Catholyte Solution: 1.4 M $KHCO_3$

Catholyte flow rate: 3.0 LPM (upflow)
Catholyte flow velocity: 0.068 ft/sec
Applied cell current: 6 amps (6,000 mA)
Catholyte pH range: Increasing slowly from around a pH of 7.62 linearly with time during the run to a final pH of 7.73

Results:

[0104]

Cell voltage range: Started at 3.84 volts, and slowly declined to 3.42 volts
Run time: Batch mode, 19 hours

[0105] The formate Faradaic efficiency started at about 65% and declined after 10 hours to 36% and to about 18.3% after 19 hours. The final formate concentration ended up at 20,500 ppm at the end of the 19 hour run. See Figures 11 and 12.

EXAMPLE 10

[0106] The same cell as in Examples 1, 2, and 3 was used, except for using 805 gm of indium coated tin shot (3 mm diameter) media and with a 0.010 inch (0.0254 cm) thickness indium foil mounted on the 316L SS back conductor plate using a conductive silver epoxy as the cathode. The cathode compartment thickness was 1.25 inches and the system was operated in a batch mode with no feed input. Carbon dioxide was sparged to saturate the solution in the catholyte disengager. The tin shot was electrolessly plated with indium in the same method as used in Examples 1 - 4 on the tincoated copper mesh. The indium coating was estimated to be about 0.5 - 1.0 microns in thickness.

Indium-Coated Tin Shot Packed Bed Cathode Detail:

[0107]

Weight: 890.5 gm, indium coating on tin shot
Indium coated tin shot: 3 mm average size
Total compartment volume: 369 cm^3
Calculated tin bead surface area: 4498 cm^2
Packed bed cathode specific surface area: 12.2 cm^2/cm^3
Packed bed void volume: 34.6%

[0108] In this test run, the system was operated with a catholyte composition containing 1.40 molar potassium bicarbonate (120 gm/L $KHCO_3$), which was sparged with CO_2 to an ending pH of about 8.0

[0109] The cell was operated in a batch condition with no overflow and a sample of the catholyte loop was collected for formate concentration analysis periodically.

Operating Conditions:

[0110]

Batch Catholyte Recirculation Run
Anolyte Solution: 0.92 M H_2SO_4
Catholyte Solution: 1.4 M $KHCO_3$
Catholyte flow rate: 3.0 LPM (upflow)
Catholyte flow velocity: 0.068 ft/sec
Applied cell current: 6 amps (6,000 mA)
Catholyte pH range: Decreased slowly from around a pH of 7.86 linearly with time during the run to a final pH of 5.51

Results:

[0111]

Cell voltage range: Started at 3.68 volts, and slowly declined to 3.18 volts

Run time: Batch mode, 24 hours

[0112] The formate Faradaic efficiency started at about 100% and varied between 60% to 85%, ending at about 60% after 24 hours. The final formate concentration ended up at about 60,000 ppm at the end of the 24 hour run. Dilution error of the samples at the high formate concentrations may have provided the variability seen in the yield numbers. See Figures 13 and 14.

EXAMPLE 11

[0113] The same cell as in Examples 1, 2, and 3 was used with a newly prepared indium on tin electrocatalyst coating on a copper mesh cathode. The prepared cathode had calculated surface areas of about 3,171 cm^2, for an area about 31 times the flat cathode plate area, with a 91% void volume, and specific surface area of 12.3 cm^2/cm^3.

[0114] In this test run, the system was operated with a catholyte composition containing 1.40 M potassium bicarbonate (120 gm/L $KHCO_3$), which was sparged with CO_2 to an ending pH of 7.8 before being used.

[0115] The cells were operated in a recirculating batch mode for the first 8 hours of operation to get the catholyte formate ion concentration up to about 20,000 ppm, and then a fresh feed of 1.4 M potassium bicarbonate was metered into the catholyte at a feed rate of about 1.2 mL/min. The overflow volume was collected and volume measured, and the overflow and catholyte loop sample were sampled and analyzed for formate by ion chromatography.

Operating Conditions:

[0116]

Cathode: Electroless indium on tin on a copper mesh substrate
Continuous Feed with Catholyte Recirculation Run - 11.5 days
Anolyte Solution: 0.92 M H_2SO_4
Catholyte Solution: 1.4 M $KHCO_3$
Catholyte flow rate: 3.2 LPM
Catholyte flow velocity: 0.09 ft/sec
Applied cell current: 6 amps (6,000 mA)

Results:

[0117]

Cell voltage versus time: FIG. 15 illustrates results of cell voltage versus time, displaying a stable operating voltage of about 3.45 volts over the 11.5 days after the initial start-up.
Continuous Run time: 11.5 days
Formate Concentration Versus Time: FIG. 16 shows results of the formate concentration versus time.
Formate Faradaic yield: FIG. 17 illustrates the calculated formate current efficiency versus time measuring the formate yield from the collected samples.
Final formate concentration: About 28,000 ppm.
Catholyte pH: FIG. 18 illustrates the catholyte pH change over the 11.5 days, which slowly declined from a pH of 7.8 to a pH value of 7.5. The feed rate was not changed during the run, but could have been slowly increased or decreased to maintain a constant catholyte pH in any optimum operating pH range.

EXAMPLE 12

[0118] The same cell as in Examples 1, 2, and 3 was used with a newly prepared indium on tin electrocatalyst coating on a copper mesh cathode. The prepared cathode had calculated surface areas of about 3,171 cm^2, for an area about 31 times the flat cathode plate area, with a 91% void volume, and specific surface area of 12.3 cm^2/cm^3.

[0119] In this test run, the system was operated with a catholyte composition containing 1.40 M potassium bicarbonate (120 gm/L $KHCO_3$), which was sparged with CO_2 to an ending pH of 7.8 before being used.

[0120] The cells were operated in a recirculating batch mode for the first 8 hours of operation to get the catholyte formate ion concentration up to about 20,000 ppm, and then a fresh feed of 1.4 M potassium bicarbonate was metered into the catholyte at a feed rate of about 1.2 mL/min. The overflow volume was collected and volume measured, and the overflow and catholyte loop sample were sampled and analyzed for formate by ion chromatography.

Operating Conditions:

[0121]

Cathode: Electroless indium on tin on a copper mesh substrate
Continuous Feed with Catholyte Recirculation Run - 21 days
Anolyte Solution: 0.92 M H_2SO_4
Catholyte Solution: 1.4 M $KHCO_3$
Catholyte flow rate: 3.2 LPM
Catholyte flow velocity: 0.09 ft/sec
Applied cell current: 6 amps (6,000 mA)

Results:

[0122]

Cell voltage versus time: The cell showed a higher operating voltage of about 4.40 volts, higher than all of our other cells, because of an inadequate electrical contact pressure of the cathode against the indium foil conductor back plate. The cell maintained operation for an extended run.
Continuous Run time: 21 days

[0123] Formate Faradaic yield: FIG. 19 illustrates calculated formate current efficiency versus time measuring the formate yield from the collected samples. The formate Faradaic current efficiency declined down into the 20% range after 16 days.

[0124] Formate Concentration Versus Time: FIG. 20 illustrates results of the formate concentration versus time. On day 21, 0.5 gm of indium (III) carbonate was added to the catholyte while the cell was still operating at the 6 ampere operating rate. The formate concentration in the catholyte operating loop was 11,330 ppm before the indium addition, which increased to 13,400 ppm after 8 hours, and increased to 14,100 ppm after 16 hours when the unit was shut down after 21 days of operation.

[0125] Catholyte pH: FIG. 21 illustrates the catholyte pH change over the continuous operation period, which operated in the 7.6 to 7.7 pH range except for an outlier data point near day 16 when the feed pump had stopped pumping. The feed rate was not changed during the run, but could have been increased or decreased to maintain a constant pH operation in an optimum range.

Claims

1. A method for electrochemical reduction of carbon dioxide into products, comprising:

(A) introducing an acidic anolyte to a first compartment of a first electrochemical cell, the first compartment including an anode;
(B) introducing a catholyte including an alkali metal bicarbonate to a second compartment of the first electrochemical cell, the catholyte saturated with carbon dioxide, the second compartment including a high surface area cathode, the high surface area cathode having a specific surface area of greater than 2 cm^2/cm^3 and including an indium coating and having a void volume of between 30% to 98%, at least a portion of the bicarbonate-based catholyte being recycled;
(C) applying an electrical potential between the anode and the cathode sufficient to reduce the carbon dioxide to an alkali metal formate;
(D) introducing the alkali metal formate to an ion exchange compartment of a second electrochemical cell;
(E) applying an electrical potential between an anode of the second electrochemical cell and a cathode of the second electrochemical cell sufficient to produce at least formic acid and an alkali metal hydroxide; and
(F) introducing the alkali metal hydroxide with carbon dioxide to generate at least a portion of the alkali metal bicarbonate introduced to the second compartment of the first electrochemical cell.

2. The method of claim 1, further comprising:

separating the alkali metal formate from the alkali metal bicarbonate of the catholyte of the first electrochemical cell with a nano-filtration system.

3. The method of claim 1, wherein separating the alkali metal formate from the alkali metal bicarbonate of the catholyte of the first electrochemical cell with a nano-filtration system comprises:

introducing the alkali metal bicarbonate of the catholyte to an alkali metal hydroxide to convert at least a portion of the alkali metal bicarbonate to an alkali metal carbonate; and
separating the alkali metal carbonate from the alkali metal formate with a nano-filtration unit.

4. The method of claim 1, further comprising:

introducing the alkali metal carbonate with the alkali metal hydroxide and with carbon dioxide to generate at least a portion of the alkali metal bicarbonate introduced to the second compartment of the first electrochemical cell.

5. The method of claim 1, wherein the acidic anolyte includes sulfuric acid.

6. The method of claim 1, further comprising:

generating a halogen selected from the group consisting of F_2, Cl_2, Br_2, and I_2 in at least one of the first compartment of the first electrochemical cell and the first compartment of the second electrochemical cell, wherein the method optionally further comprises reacting the halogen with an organic compound to produce a halogenated product, and wherein optionally the halogen is bromine.

7. The method of any one of the preceding claims, wherein a homogenous heterocyclic catalyst is utilized in the catholyte of the first electrochemical cell.

8. The method of any one of the preceding claims, wherein the homogenous heterocyclic catalyst includes one or more of 4-hydroxy pyridine, adenine, a heterocyclic amine containing sulfur, a heterocyclic amine containing oxygen, an azole, a benzimidazole, a bipyridine, furan, an imidazole, an indole, a lutidine, methylimidazole, an oxazole, phenanthroline, pterin, pteridine, a pyridine, pyrrole, quinoline, or a thiazole, and mixtures thereof.

9. The method of any one of the preceding claims, wherein the cathode of the first electrochemical cell includes a tin coating on a high surface area copper substrate with a top layer/coating of indium.

10. The method of any one of the preceding claims, further comprising operating the first electrochemical cell at a pressure exceeding atmospheric pressure.

11. The method of any one of the preceding claims, wherein the anode of the first electrochemical cell includes an electrocatalytic coating including ruthenium oxide, iridium oxide, platinum, platinum oxides, gold or gold oxide.

Patentansprüche

1. Verfahren zur elektrochemischen Reduktion von Kohlendioxid zu Produkten, umfassend:

(A) Einführen eines sauren Anolyten in eine erste Kammer einer ersten elektrochemischen Zelle, wobei die erste Kammer eine Anode enthält;
(B) Einführen eines Katholyten, der ein Alkalimetallbicarbonat enthält, in eine zweite Kammer der ersten elektrochemischen Zelle, wobei der Katholyt mit Kohlendioxid gesättigt ist, wobei die zweite Kammer eine Kathode mit hoher Oberfläche enthält, wobei die Kathode mit hoher Oberfläche eine spezifische Oberfläche von größer als 2 cm^2/cm^3 aufweist und eine Indiumbeschichtung aufweist und ein Hohlraumvolumen zwischen 30 % und 98 % aufweist, wobei wenigstens ein Teil des Katholyten auf Bicarbonatbasis recycelt ist;
(C) Anlegen eines elektrischen Potentials zwischen der Anode und der Kathode, das ausreicht, um das Kohlendioxid zu einem Alkalimetallformiat zu reduzieren;
(D) Einführen des Alkalimetallformiats in eine Ionenaustauschkamnmer einer zweiten elektrochemischen Zelle;
(E) Anlegen eines elektrischen Potentials zwischen einer Anode der zweiten elektrochemischen Zelle und einer Kathode der zweiten elektrochemischen Zelle, das ausreicht, um wenigstens Ameisensäure und ein Alkalimetallhydroxid zu erzeugen; und
(F) Einführen des Alkalimetallhydroxids mit Kohlendioxid, um wenigstens einen Teil des in die zweite Kammer

der ersten elektrochemischen Zelle eingeführten Alkalimetallbicarbonats zu erzeugen.

2. Verfahren gemäß Anspruch 1, ferner umfassend:

Abtrennen des Alkalimetallformiats von dem Alkalimetallbicarbonat des Katholyten der ersten elektrochemischen Zelle durch ein Nanofiltrationssystem.

3. Verfahren gemäß Anspruch 1, wobei das Abtrennen des Alkalimetallformiats von dem Alkalimetallbicarbonat des Katholyten der ersten elektrochemischen Zelle durch ein Nanofiltrationssystem umfasst:

Einführen des Alkalimetallbicarbonats des Katholyten zu einem Alkalimetallhydroxid, um wenigstens einen Teil des Alkalimetallbicarbonats in ein Alkalimetallcarbonat umzuwandeln; und
Abtrennen des Alkalimetallcarbonats von dem Alkalimetallformiat durch eine Nanofiltrationseinheit.

4. Verfahren gemäß Anspruch 1, ferner umfassend:

Einführen des Alkalimetallbicarbonats mit dem Alkalimetallhydroxid und mit Kohlendioxid, um wenigstens einen Teil des in die zweite Kammer der ersten elektrochemischen Zelle eingeführten Alkalimetallbicarbonats zu erzeugen.

5. Verfahren gemäß Anspruch 1, wobei der saure Anolyt Schwefelsäure enthält.

6. Verfahren gemäß Anspruch 1, ferner umfassend:

Erzeugen eines Halogens ausgewählt aus der Gruppe bestehend aus F_2, Cl_2, Br_2 und I_2 in wenigstens einer von der ersten Kammer der ersten elektrochemischen Zelle und der ersten Kammer der zweiten elektrochemischen Zelle, wobei das Verfahren gegebenenfalls ferner Umsetzen des Halogens mit einer organischen Verbindung umfasst, um ein halogeniertes Produkt zu erzeugen, wobei das Halogen gegebenenfalls Brom ist.

7. Verfahren gemäß einem der vorstehenden Ansprüche, wobei in dem Katholyten der ersten elektrochemischen Zelle ein homogener heterocyclischer Katalysator eingesetzt wird.

8. Verfahren gemäß einem der vorstehenden Ansprüche, wobei der homogene heterocyclische Katalysator eines oder mehrere von 4-Hydroxypyridin, Adenin, einem heterocyclischen Amin, das Schwefel enthält, einem heterocyclischen Amin, das Sauerstoff enthält, einem Azol, einem Benzimidazol, einem Bipyridin, Furan, einem Imidazol, einem Indol, einem Lutidin, Methylimidazol, einem Oxazol, Phenanthrolin, Pterin, Pteridin, einem Pyridin, Pyrrol, Chinolin oder einem Thiazol oder ein Gemisch davon umfasst.

9. Verfahren gemäß einem der vorstehenden Ansprüche, wobei die Kathode der ersten elektrochemischen Zelle eine Zinnbeschichtung auf einem Kupfersubstrat mit hoher Oberfläche mit einer Deckschicht/beschichtung aus Indium umfasst.

10. Verfahren gemäß einem der vorstehenden Ansprüche, ferner umfassend Betreiben der ersten elektrochemischen Zelle bei einem Druck, der höher als der atmosphärische Druck ist.

11. Verfahren gemäß einem der vorstehenden Ansprüche, wobei die Anode der ersten elektrochemischen Zelle eine elektrokatalytische Beschichtung umfasst, die Rutheniumoxid, Iridiumoxid, Platin, Platinoxide, Gold oder Goldoxid umfasst.

Revendications

1. Procédé pour la réduction électrochimique de dioxyde de carbone en produits, comprenant :

(A) l'introduction d'un anolyte acide dans un premier compartiment d'une première cellule électrochimique, le premier compartiment comprenant une anode ;
(B) l'introduction d'un catholyte comprenant un bicarbonate de métal alcalin dans un second compartiment de la première cellule électrochimique, le catholyte étant saturé en dioxyde de carbone, le second compartiment

comprenant une cathode de surface grande, la cathode de surface grande ayant une surface spécifique supérieure à 2 cm^2/cm^3 et comprenant un revêtement d'indium et ayant un volume de vide compris entre 30 % et 98 %, au moins une partie du catholyte à base de bicarbonate étant recyclée ;
(C) l'application entre l'anode et la cathode d'un potentiel électrique suffisant pour réduire le dioxyde de carbone en un formiate de métal alcalin ;
(D) l'introduction du formiate de métal alcalin dans un compartiment d'échange d'ions d'une seconde cellule électrochimique ;
(E) l'application entre une anode de la seconde cellule électrochimique et une cathode de la seconde cellule électrochimique d'un potentiel électrique suffisant pour produire au moins de l'acide formique et un hydroxyde de métal alcalin ; et
(F) l'introduction de l'hydroxyde de métal alcalin avec du dioxyde de carbone pour produire au moins une partie du bicarbonate de métal alcalin introduit dans le second compartiment de la première cellule électrochimique.

2. Procédé selon la revendication 1, comprenant en outre :

la séparation du formiate de métal alcalin d'avec le bicarbonate de métal alcalin du catholyte de la première cellule électrochimique avec un système de nanofiltration.

3. Procédé selon la revendication 1, dans lequel la séparation du formiate de métal alcalin d'avec le bicarbonate de métal alcalin du catholyte de la première cellule électrochimique avec un système de nanofiltration comprend :

l'introduction du bicarbonate de métal alcalin du catholyte dans un hydroxyde de métal alcalin pour convertir au moins une partie du bicarbonate de métal alcalin en un carbonate de métal alcalin ; et
la séparation du carbonate de métal alcalin d'avec le formiate de métal alcalin avec une unité de nanofiltration.

4. Procédé selon la revendication 1, comprenant en outre :

l'introduction du carbonate de métal alcalin avec l'hydroxyde de métal alcalin et avec du dioxyde de carbone pour produire au moins une partie du bicarbonate de métal alcalin introduit dans le second compartiment de la première cellule électrochimique.

5. Procédé selon la revendication 1, dans lequel l'anolyte acide comprend de l'acide sulfurique.

6. Procédé selon la revendication 1, comprenant en outre :

la production d'un halogène choisi dans le groupe constitué par F_2, Cl_2, Br_2 et I_2 dans au moins l'un du premier compartiment de la première cellule électrochimique et du premier compartiment de la seconde cellule électrochimique, le procédé comprenant éventuellement en outre la réaction de l'halogène avec un composé organique pour produire un produit halogéné et dans lequel éventuellement l'halogène est le brome.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel un catalyseur hétérocyclique homogène est utilisé dans le catholyte de la première cellule électrochimique.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le catalyseur hétérocyclique homogène en comprend un ou plusieurs parmi la 4-hydroxypyridine, l'adénine, une amine hétérocyclique contenant du soufre, une amine hétérocyclique contenant de l'oxygène, un azole, un benzimidazole, une bipyridine, le furane, un imidazole, un indole, une lutidine, le méthylimidazole, un oxazole, la phénanthroline, la ptérine, la ptéridine, une pyridine, le pyrrole, la quinoléine ou un thiazole et les mélanges de ceux-ci.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel la cathode de la première cellule électrochimique comprend un revêtement d'étain sur un substrat en cuivre de surface grande avec une couche supérieure/un revêtement d'indium.

10. Procédé selon l'une quelconque des revendications précédentes, comprenant en outre le fonctionnement de la première cellule électrochimique à une pression supérieure à la pression atmosphérique.

11. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'anode de la première cellule électrochimique comprend un revêtement électrocatalytique comprenant de l'oxyde de ruthénium, de l'oxyde d'iridium,

du platine, des oxydes de platines, de l'or ou de l'oxyde d'or.

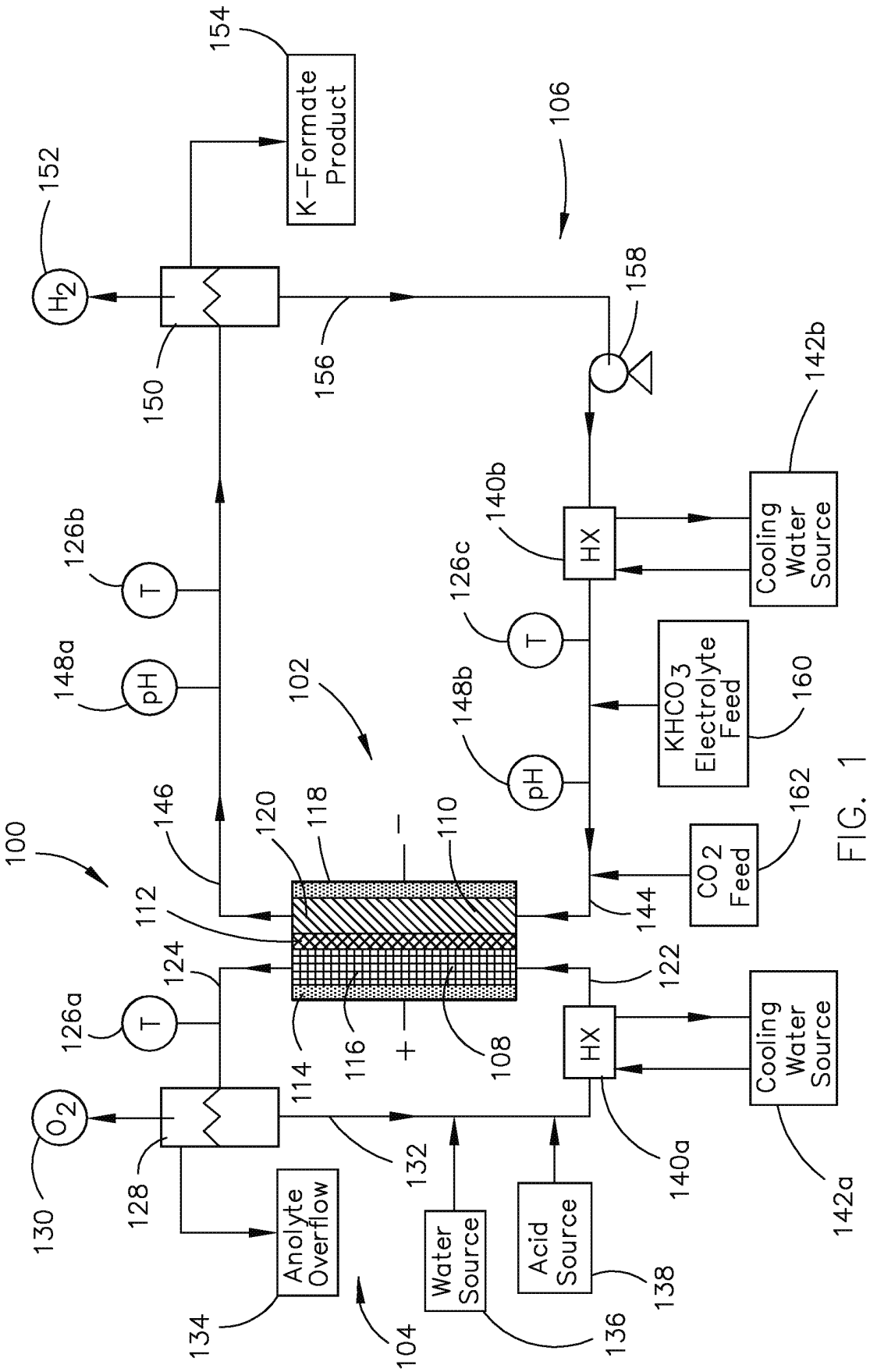

100
102
104
106
108
110
112
114
116
118
120
122
124
126a
126b
126c
128
130
132
134
136
138
140a
140b
142a
142b
144
146
148a
148b
150
152
154
156
158
160
162
K–Formate Product
H2
O2
T
pH
HX
Cooling Water Source
KHCO3 Electrolyte Feed
CO2 Feed
Anolyte Overflow
Water Source
Acid Source
+
–

FIG. 1

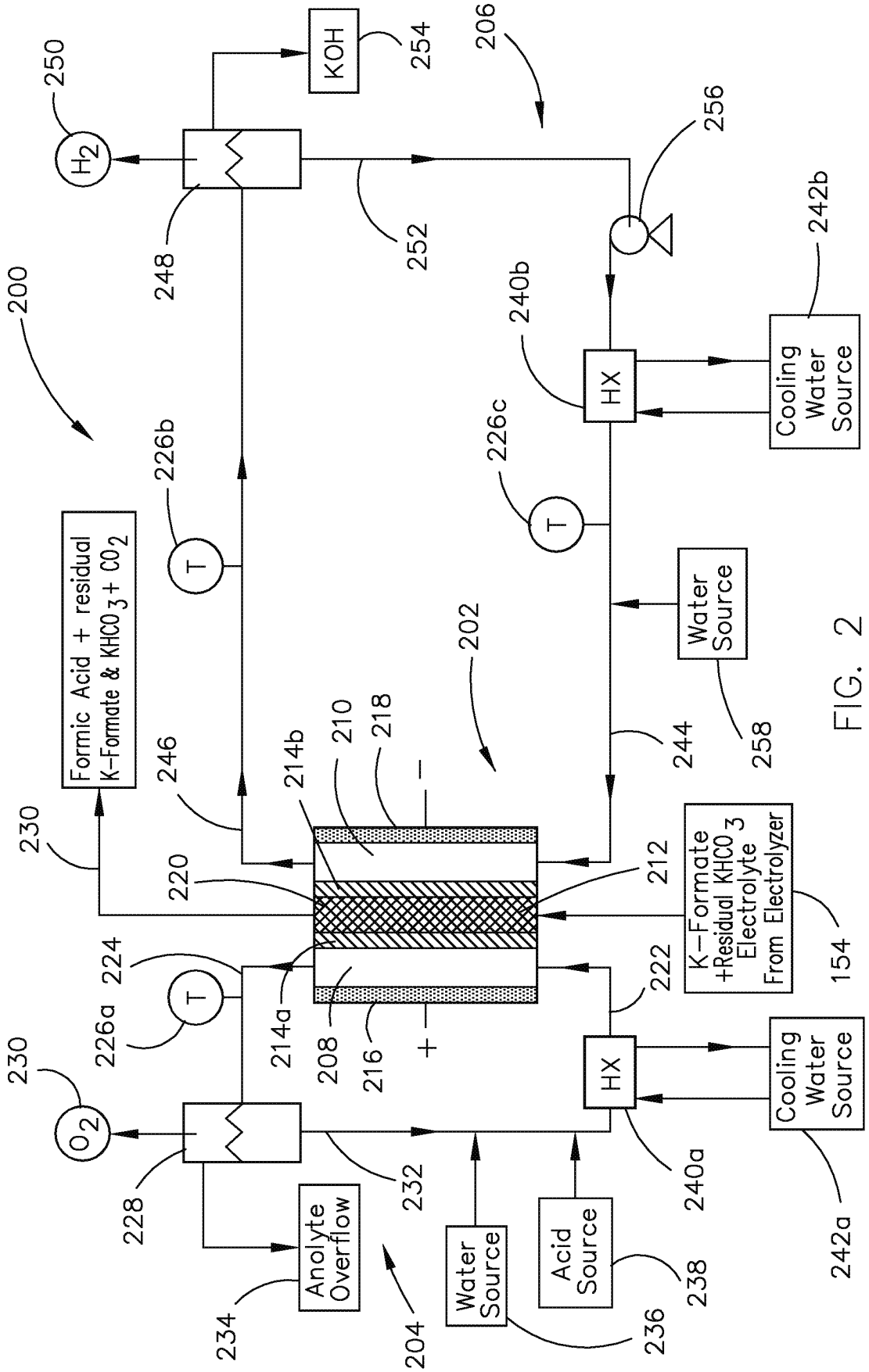

200
202
204
206
H2
250
KOH
254
248
252
256
240b
HX
Cooling Water Source
242b
226b
T
226c
T
Formic Acid + residual K-Formate & KHCO3 + CO2
230
246
214b
210
218
220
212
224
226a
T
214a
208
216
222
K-Formate +Residual KHCO3 Electrolyte From Electrolyzer
154
Water Source
258
244
O2
230
228
232
240a
HX
Cooling Water Source
242a
Anolyte Overflow
234
Water Source
236
Acid Source
238

FIG. 2

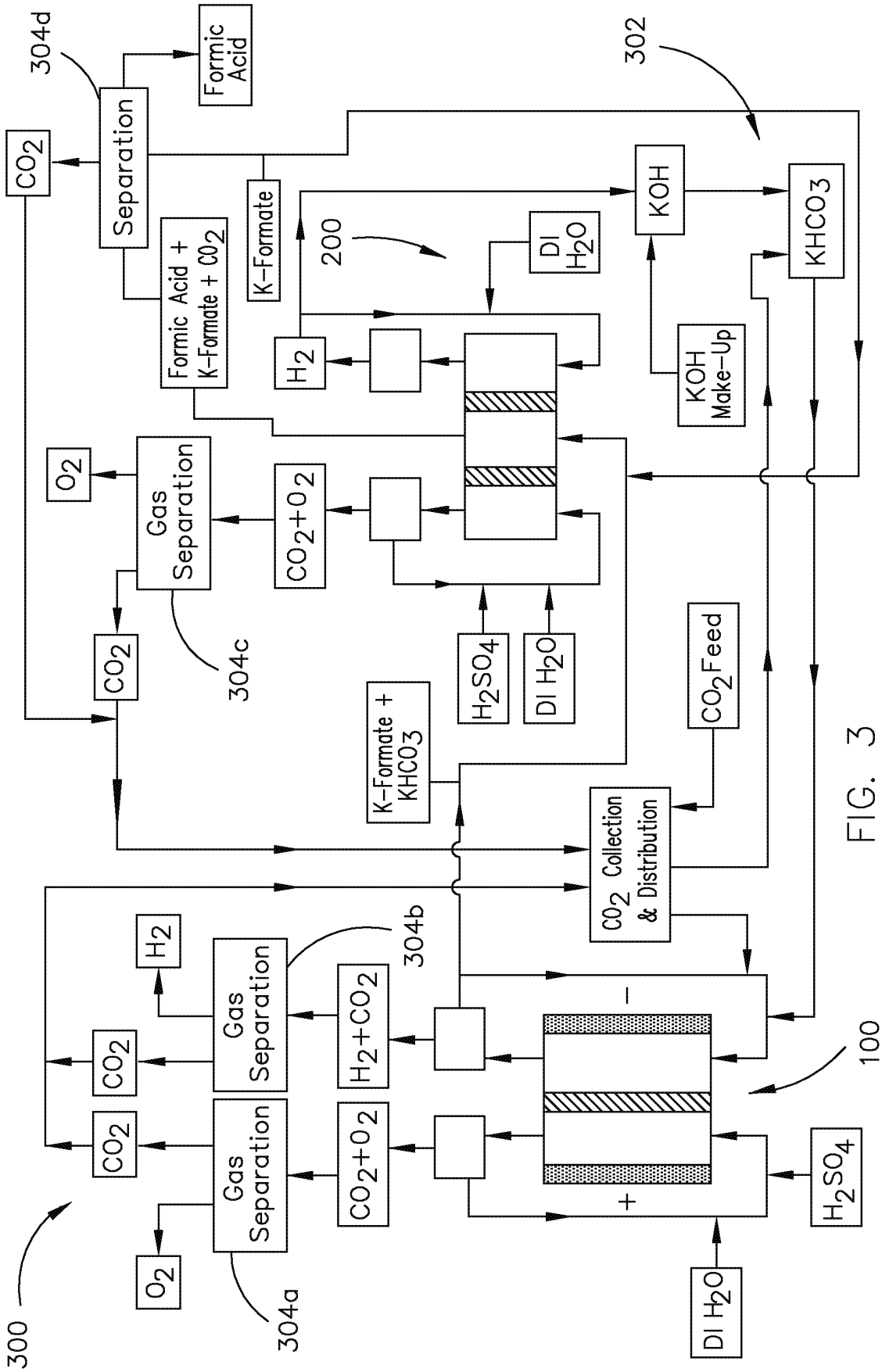

304d
Separation
Formic Acid
CO2
Formic Acid + K-Formate + CO2
K-Formate
302
KOH
KHCO3
200
DI H2O
H2
KOH Make-Up
O2
Gas Separation
CO2+O2
304c
CO2
H2SO4
DI H2O
CO2 Feed
K-Formate + KHCO3
CO2 Collection & Distribution
H2
304b
Gas Separation
H2+CO2
CO2
CO2
Gas Separation
CO2+O2
100
H2SO4
O2
304a
DI H2O
300

FIG. 3

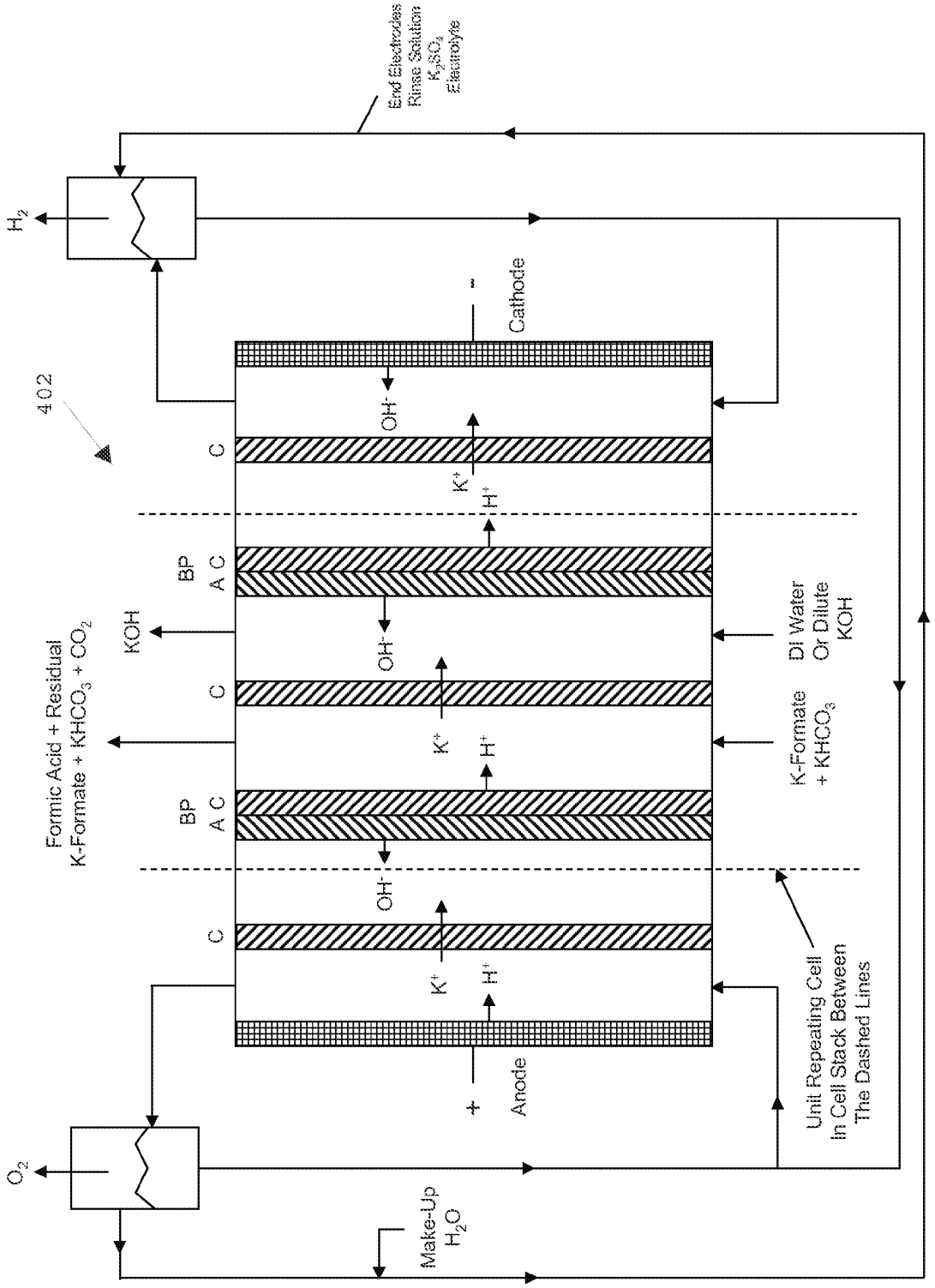

End Electrodes
Rinse Solution
K_2SO_4
Electrolyte
H_2
Cathode
402
C
OH^-
K^+
H^+
BP
A C
KOH
Di Water
Or Dilute
KOH
Formic Acid + Residual
K-Formate + $KHCO_3$ + CO_2
K-Formate
+ $KHCO_3$
Unit Repeating Cell
In Cell Stack Between
The Dashed Lines
Anode
O_2
Make-Up
H_2O
BP: Bipolar Membrane
C: Cation Exchange Membrane
A: Anion Exchange Membrane

FIG. 4

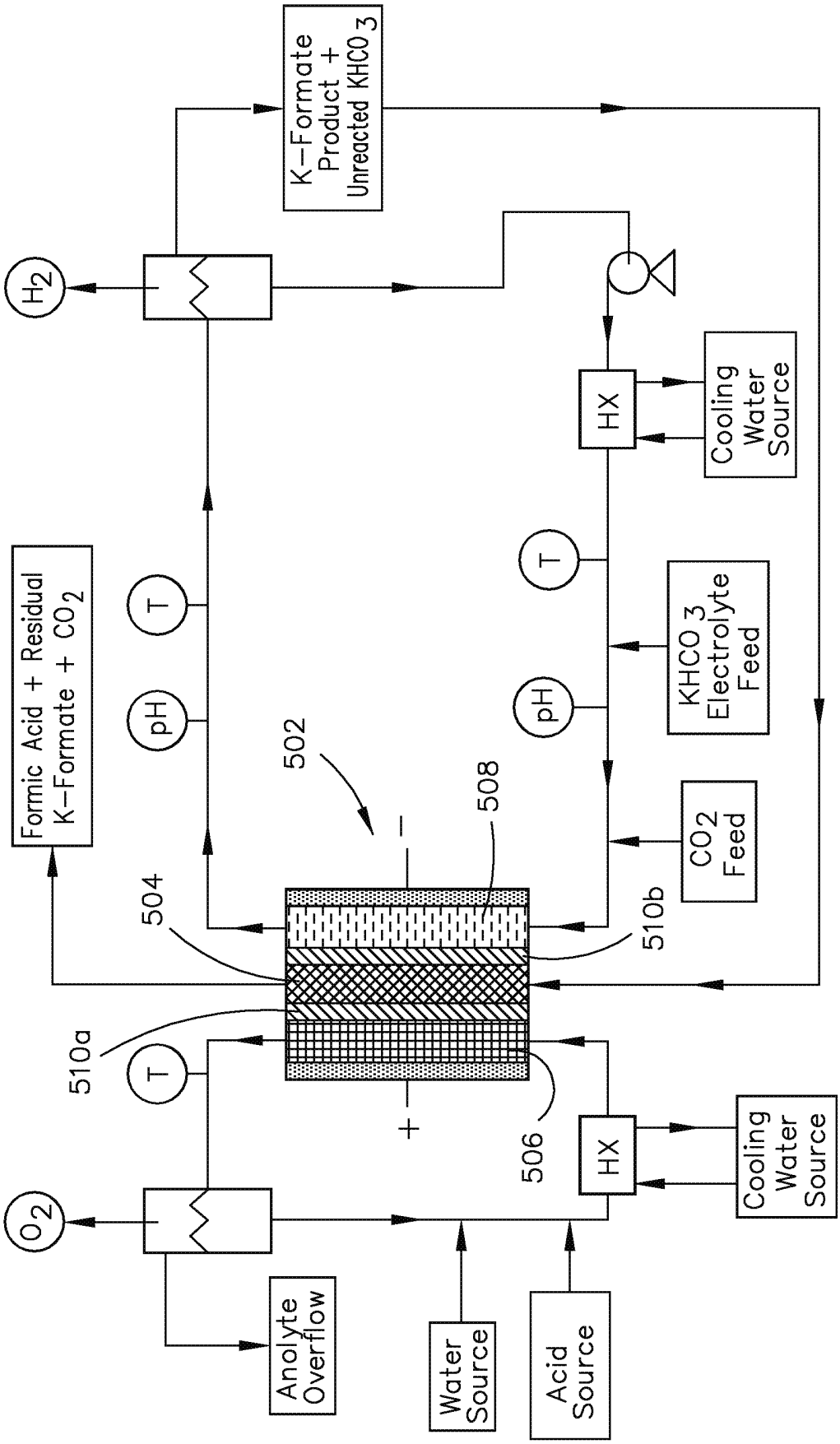

K–Formate Product + Unreacted KHCO 3
H2
HX
Cooling Water Source
T
pH
KHCO 3 Electrolyte Feed
CO2 Feed
Formic Acid + Residual K–Formate + CO2
502
508
504
510b
510a
506
+
–
O2
Anolyte Overflow
Water Source
Acid Source

FIG. 5

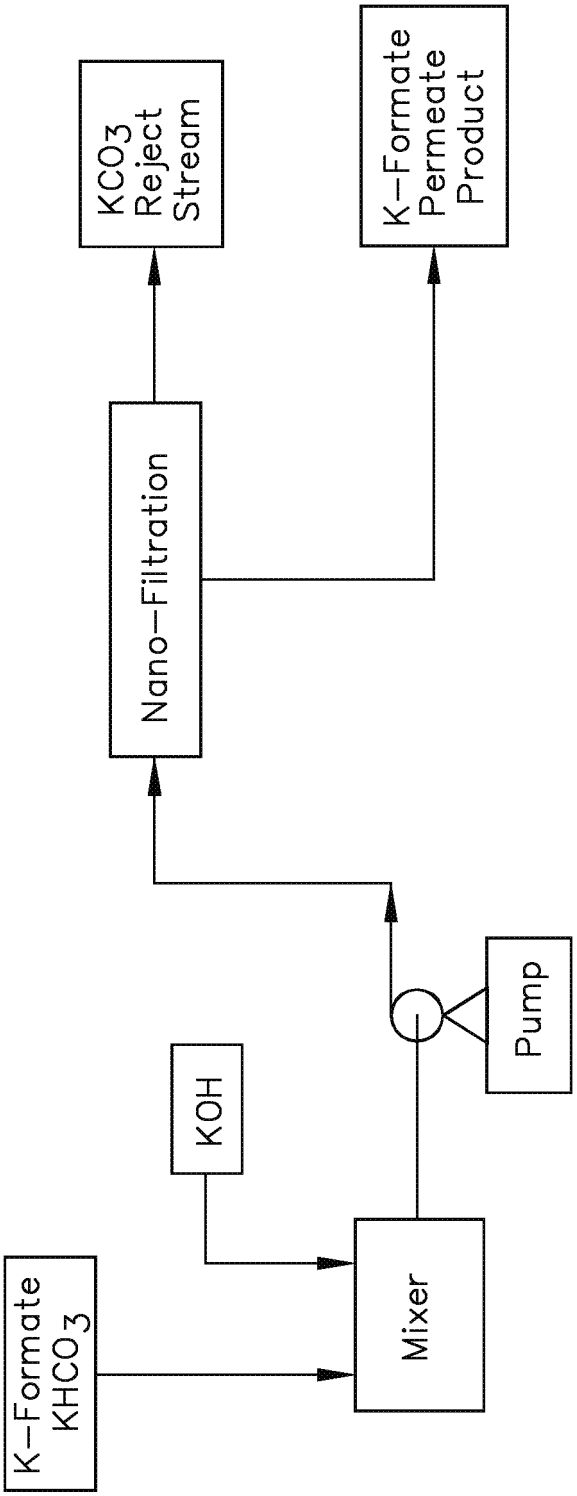

K–Formate KHCO3
KOH
Mixer
Pump
Nano–Filtration
KCO3 Reject Stream
K–Formate Permeate Product

FIG. 6

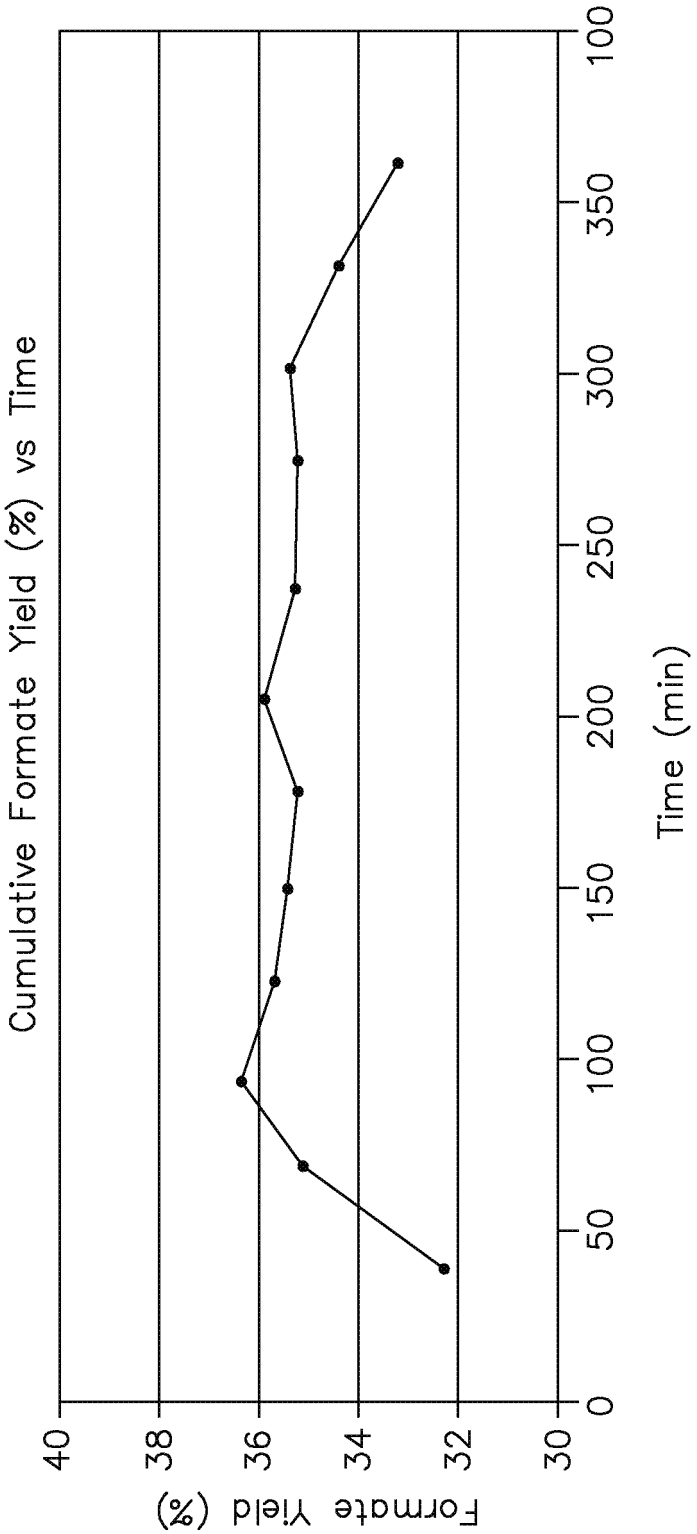

Cumulative Formate Yield (%) vs Time
Formate Yield (%)
40
38
36
34
32
30
0
50
100
150
200
250
300
350
100
Time (min)

FIG. 7

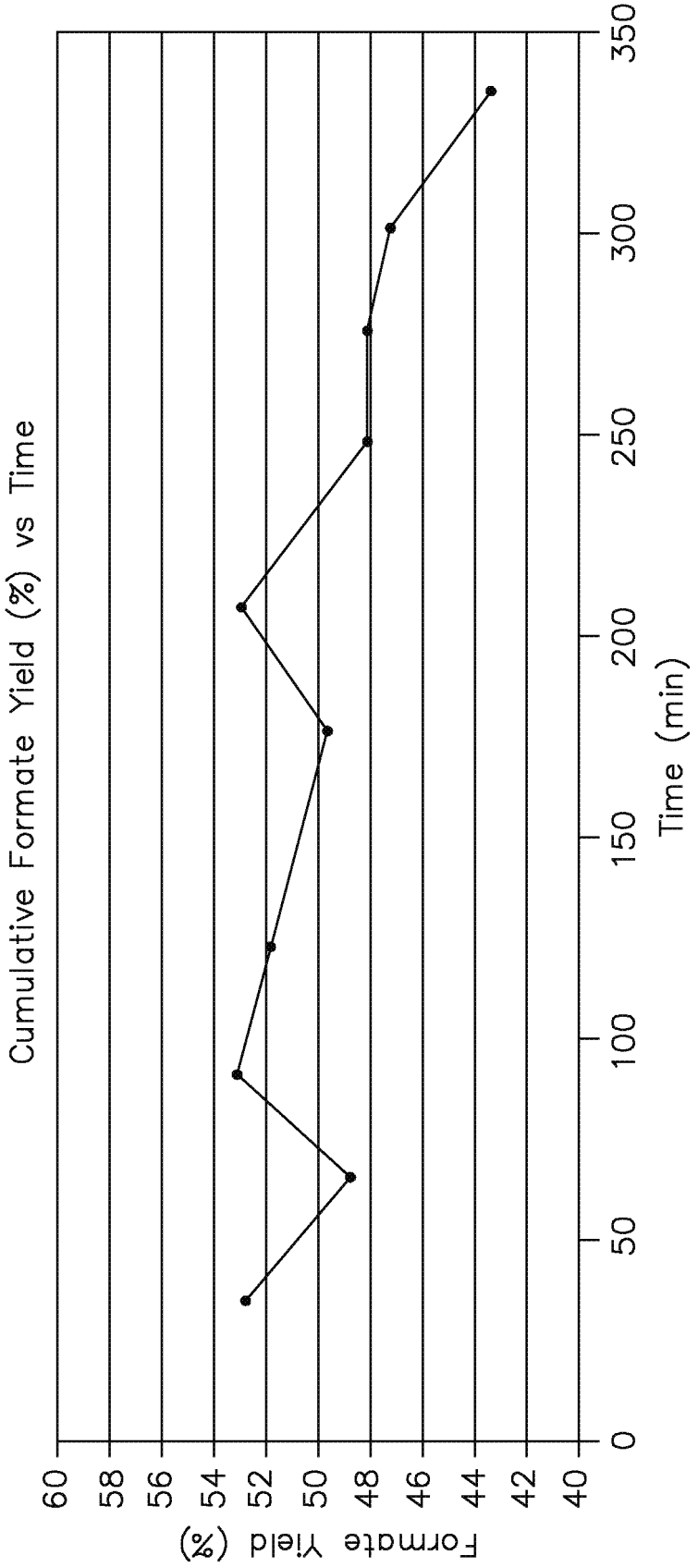

Cumulative Formate Yield (%) vs Time
Formate Yield (%)
60
58
56
54
52
50
48
46
44
42
40
0
50
100
150
200
250
300
350
Time (min)

FIG. 8

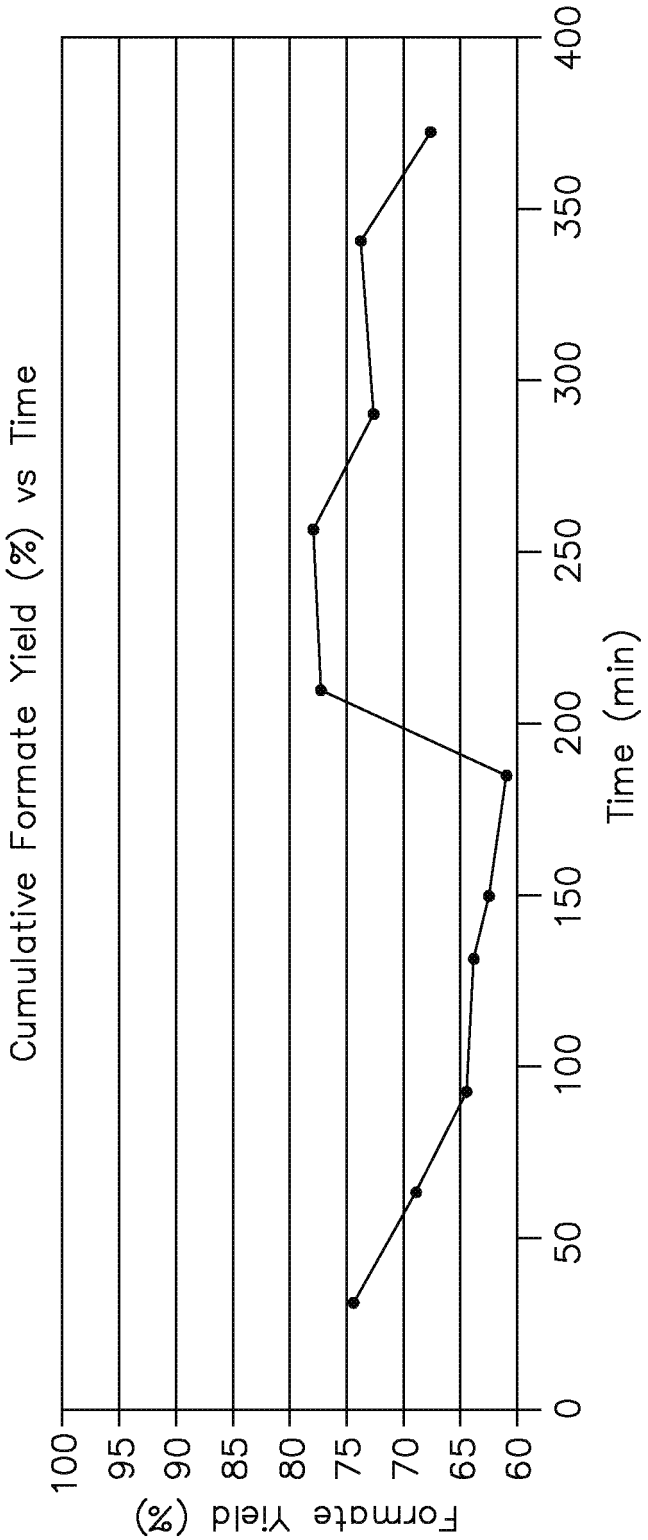

Cumulative Formate Yield (%) vs Time
Formate Yield (%)
100
95
90
85
80
75
70
65
60
0
50
100
150
200
250
300
350
400
Time (min)

FIG. 9

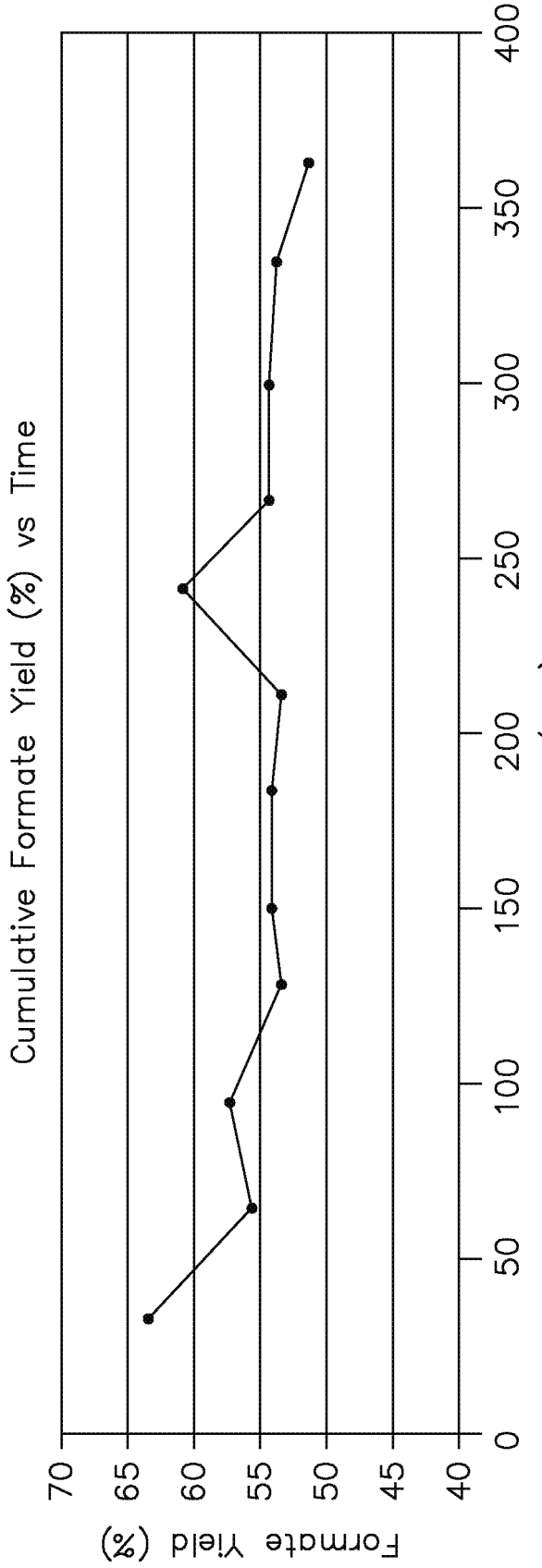

Cumulative Formate Yield (%) vs Time
Formate Yield (%)
70
65
60
55
50
45
40
0
50
100
150
200
250
300
350
400
Time (min)

FIG. 10

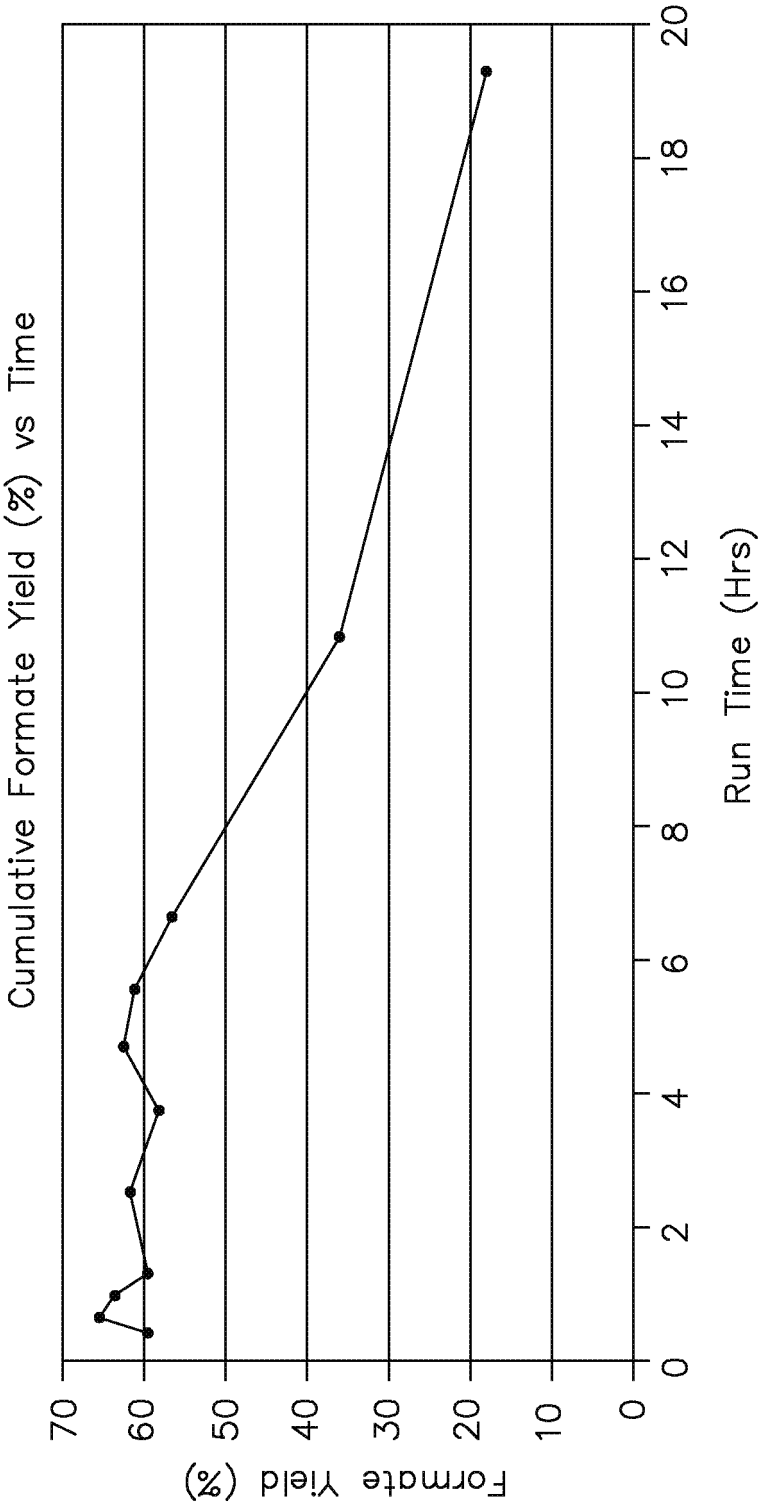

Cumulative Formate Yield (%) vs Time
Formate Yield (%)
0
10
20
30
40
50
60
70
Run Time (Hrs)
0
2
4
6
8
10
12
14
16
18
20

FIG. 11

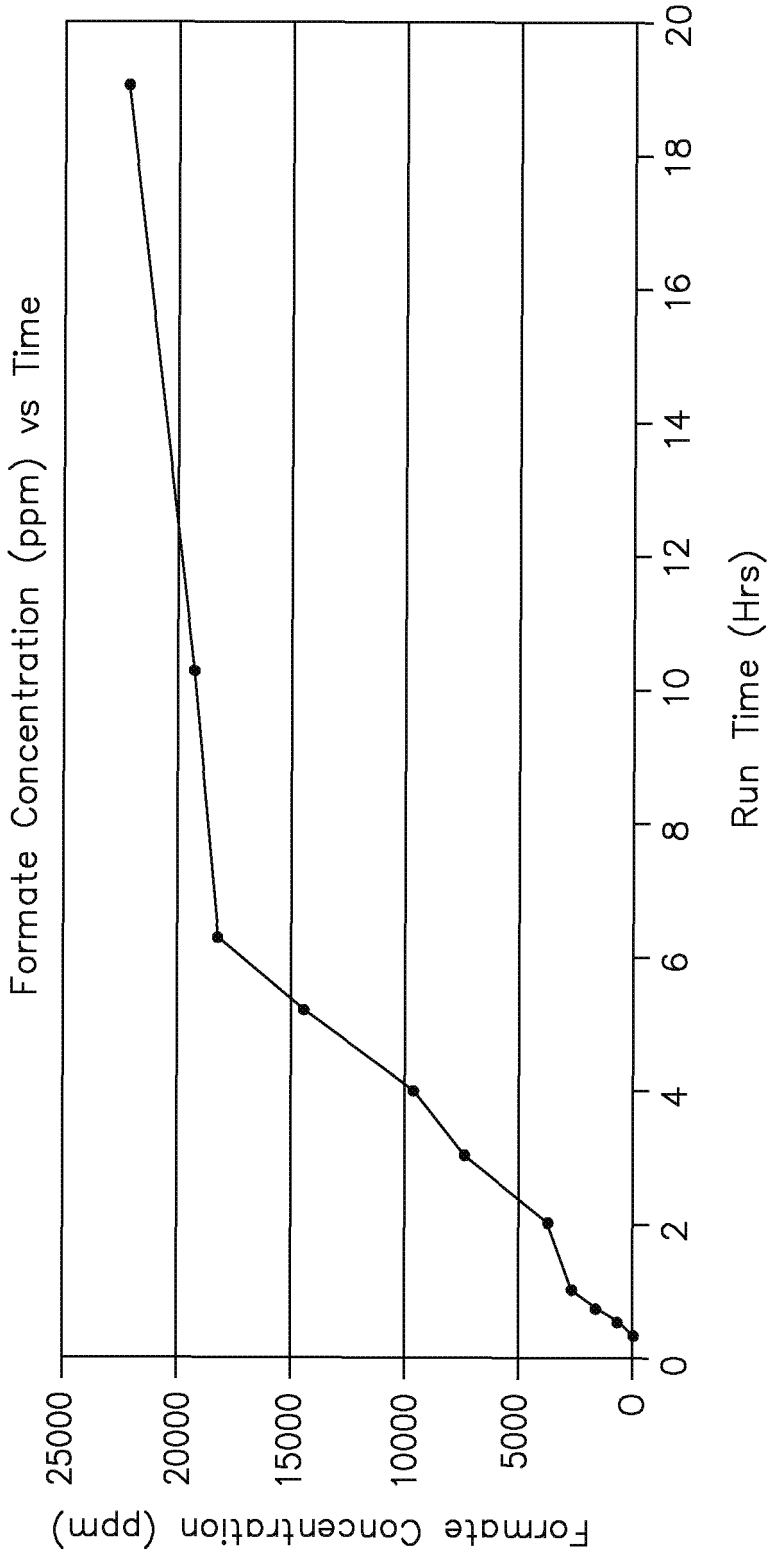

Formate Concentration (ppm) vs Time
Formate Concentration (ppm)
25000
20000
15000
10000
5000
0
0
2
4
6
8
10
12
14
16
18
20
Run Time (Hrs)

FIG. 12

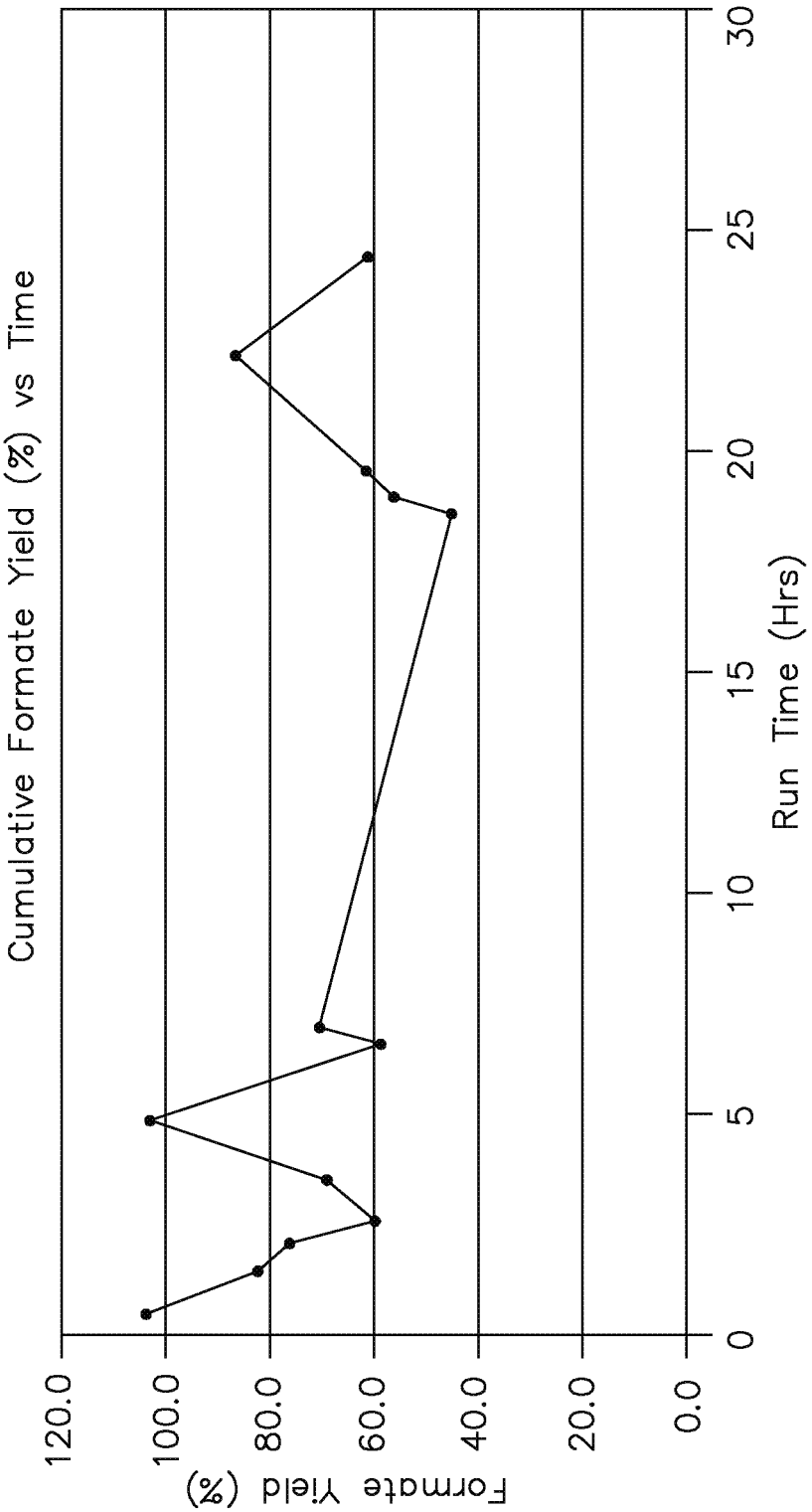

Cumulative Formate Yield (%) vs Time
Formate Yield (%)
120.0
100.0
80.0
60.0
40.0
20.0
0.0
0
5
10
15
20
25
30
Run Time (Hrs)

FIG. 13

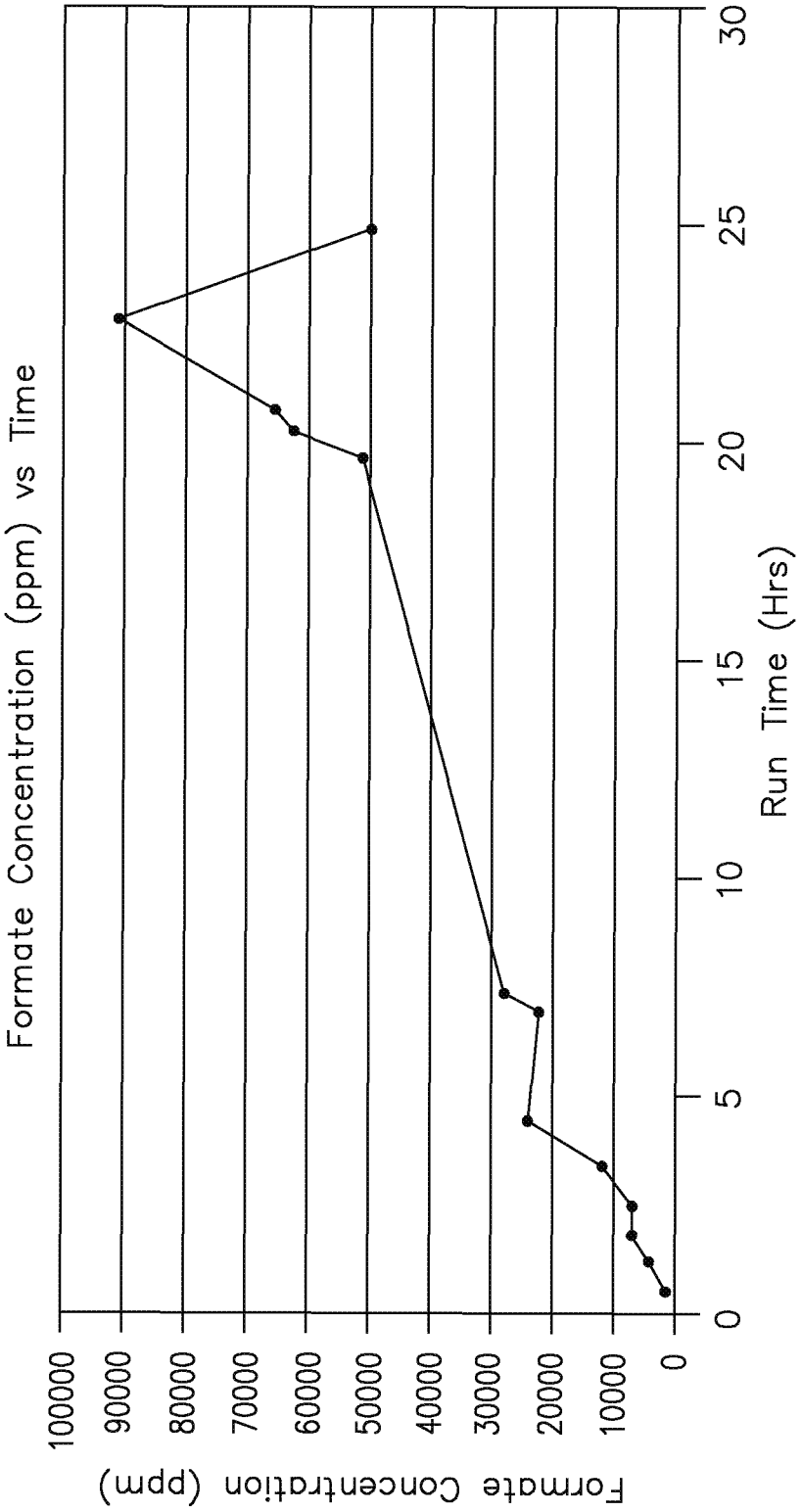

Formate Concentration (ppm) vs Time
Formate Concentration (ppm)
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
0
5
10
15
20
25
30
Run Time (Hrs)

FIG. 14

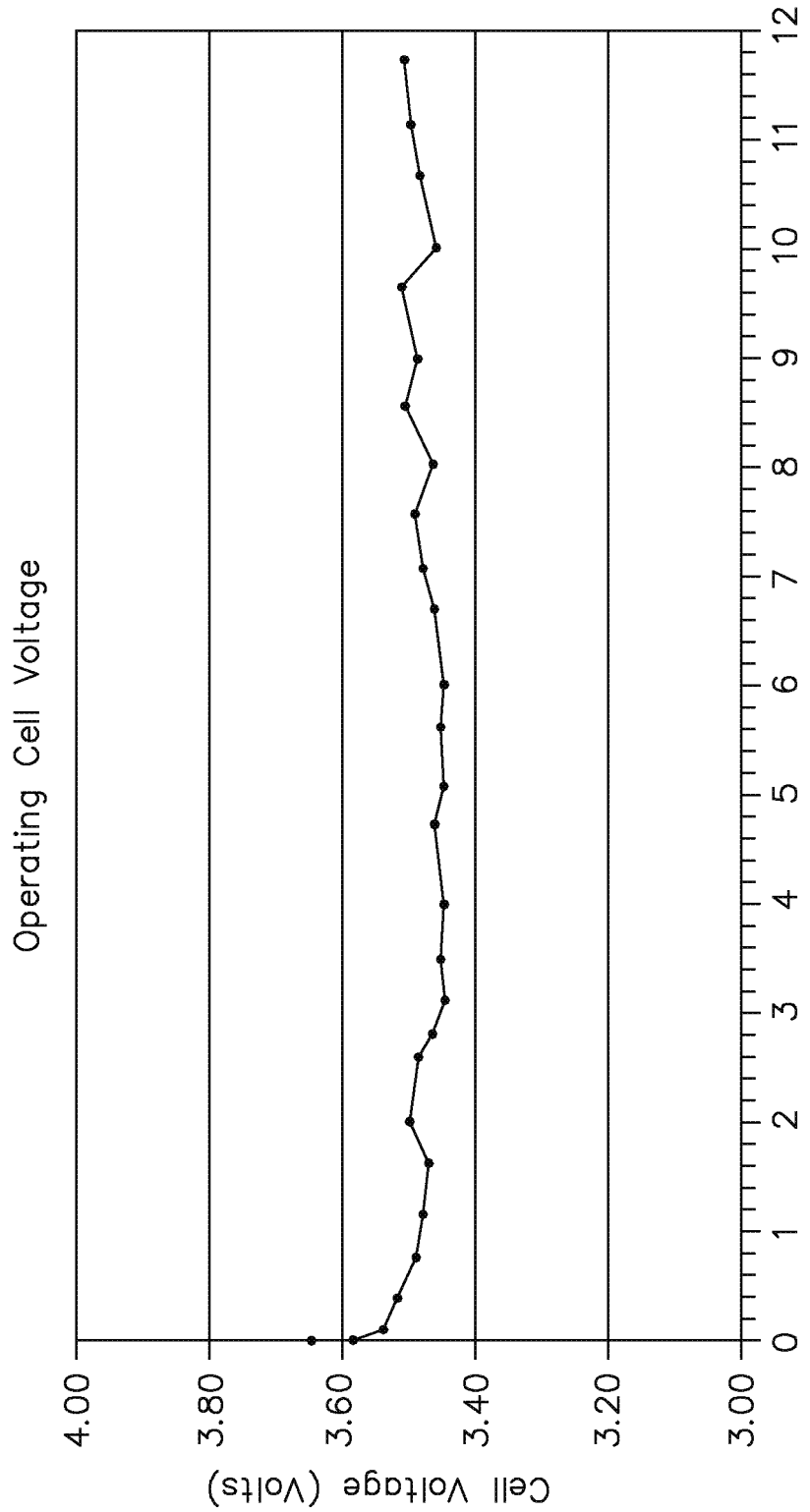

Operating Cell Voltage
Cell Voltage (Volts)
4.00
3.80
3.60
3.40
3.20
3.00
0
1
2
3
4
5
6
7
8
9
10
11
12
Time (Days)

FIG. 15

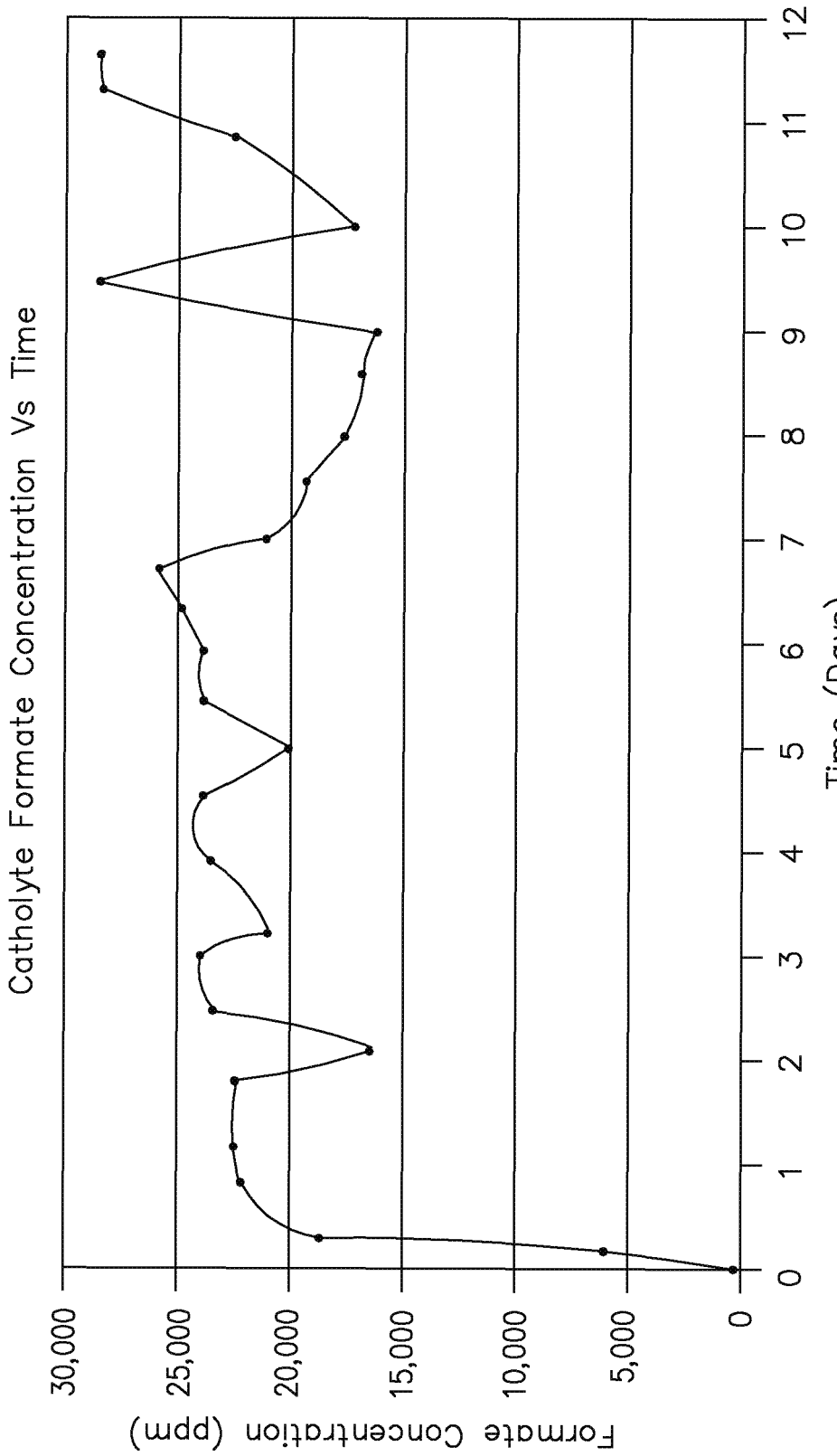

Catholyte Formate Concentration Vs Time
Formate Concentration (ppm)
30,000
25,000
20,000
15,000
10,000
5,000
0
0
1
2
3
4
5
6
7
8
9
10
11
12
Time (Days)

FIG. 16

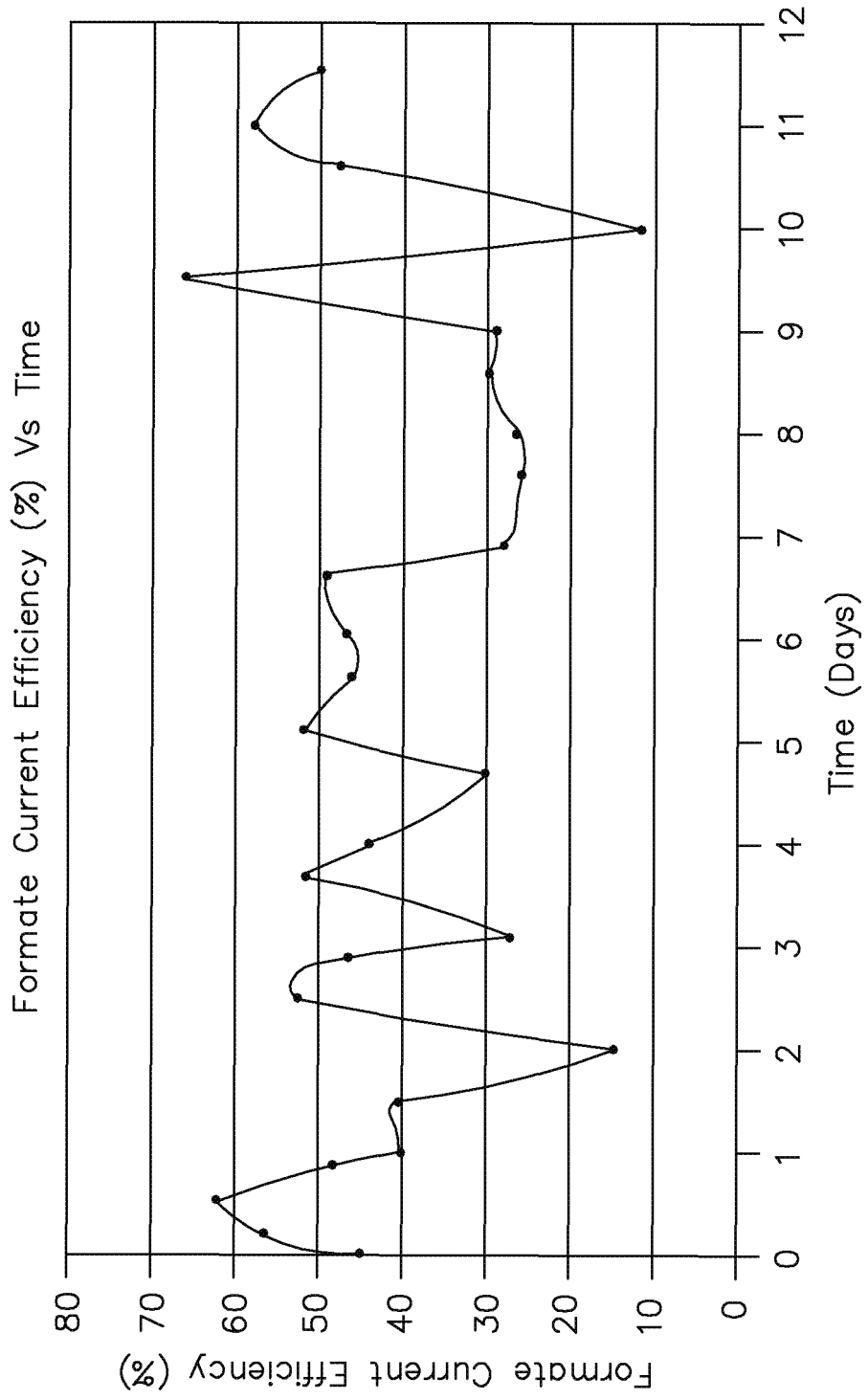

Formate Current Efficiency (%) Vs Time
Formate Current Efficiency (%)
0
10
20
30
40
50
60
70
80
Time (Days)
0
1
2
3
4
5
6
7
8
9
10
11
12

FIG. 17

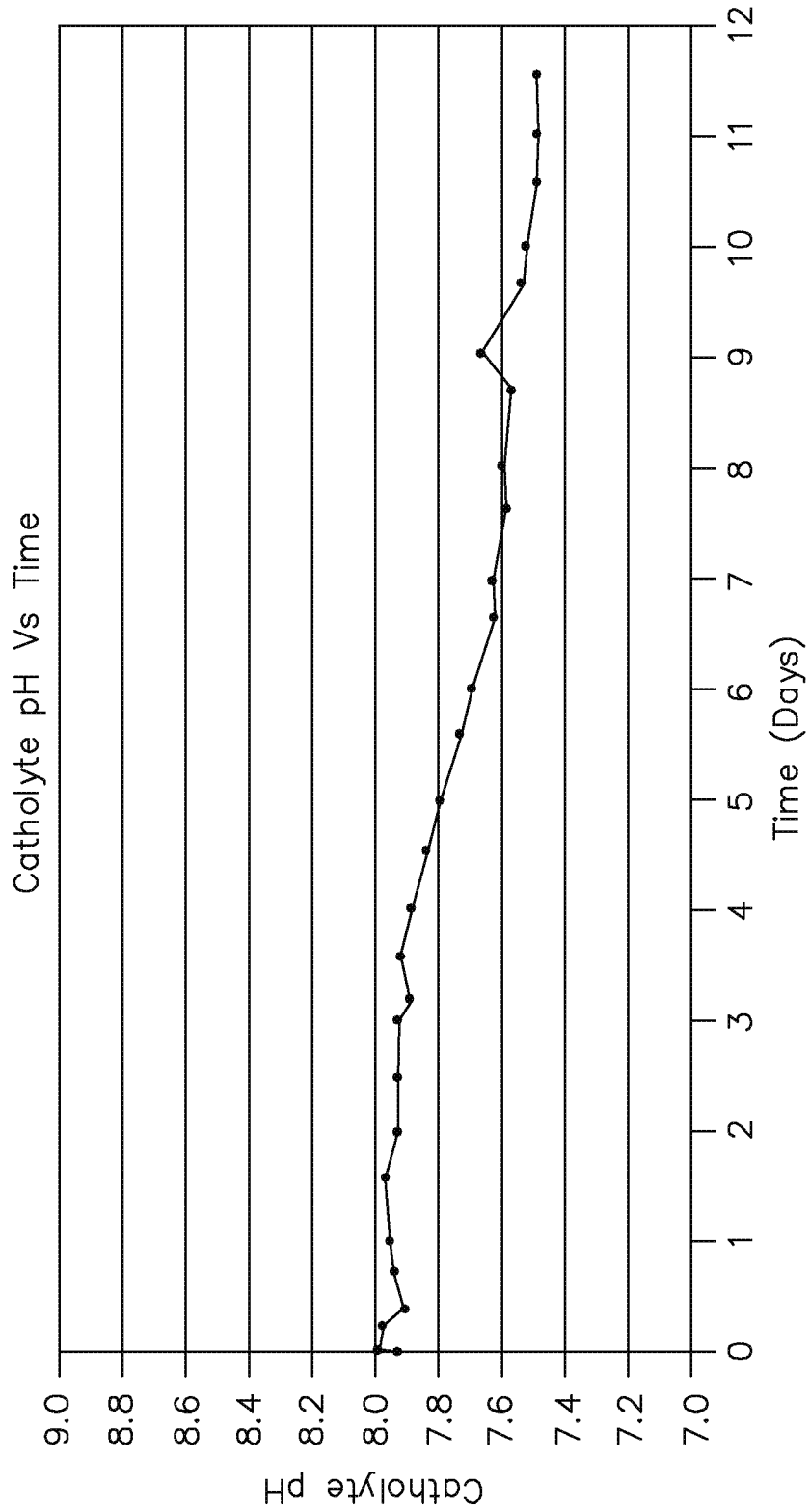

Catholyte pH Vs Time
Catholyte pH
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
0
1
2
3
4
5
6
7
8
9
10
11
12
Time (Days)

FIG. 18

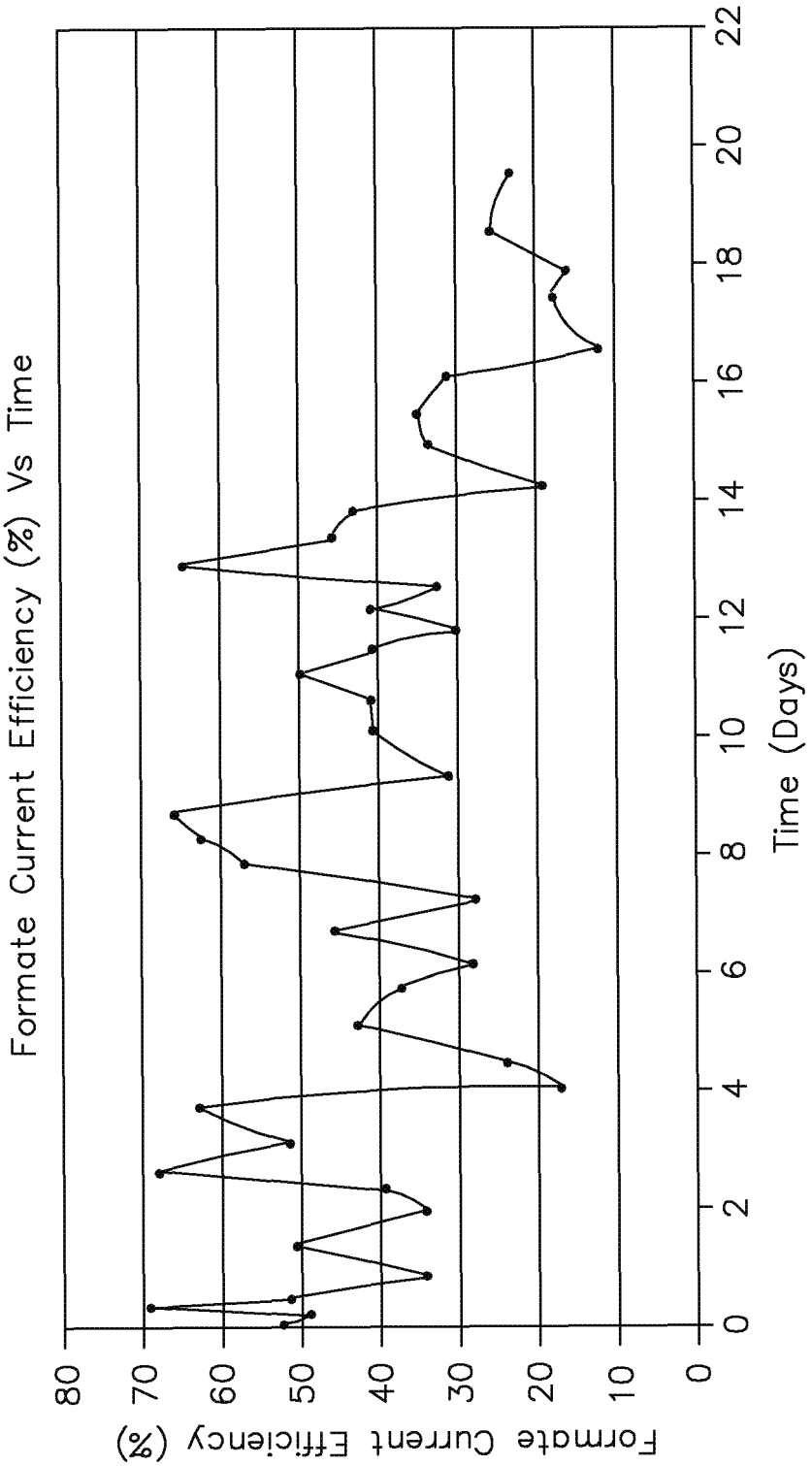

Formate Current Efficiency (%) Vs Time
Formate Current Efficiency (%)
0
10
20
30
40
50
60
70
80
Time (Days)
0
2
4
6
8
10
12
14
16
18
20
22

FIG. 19

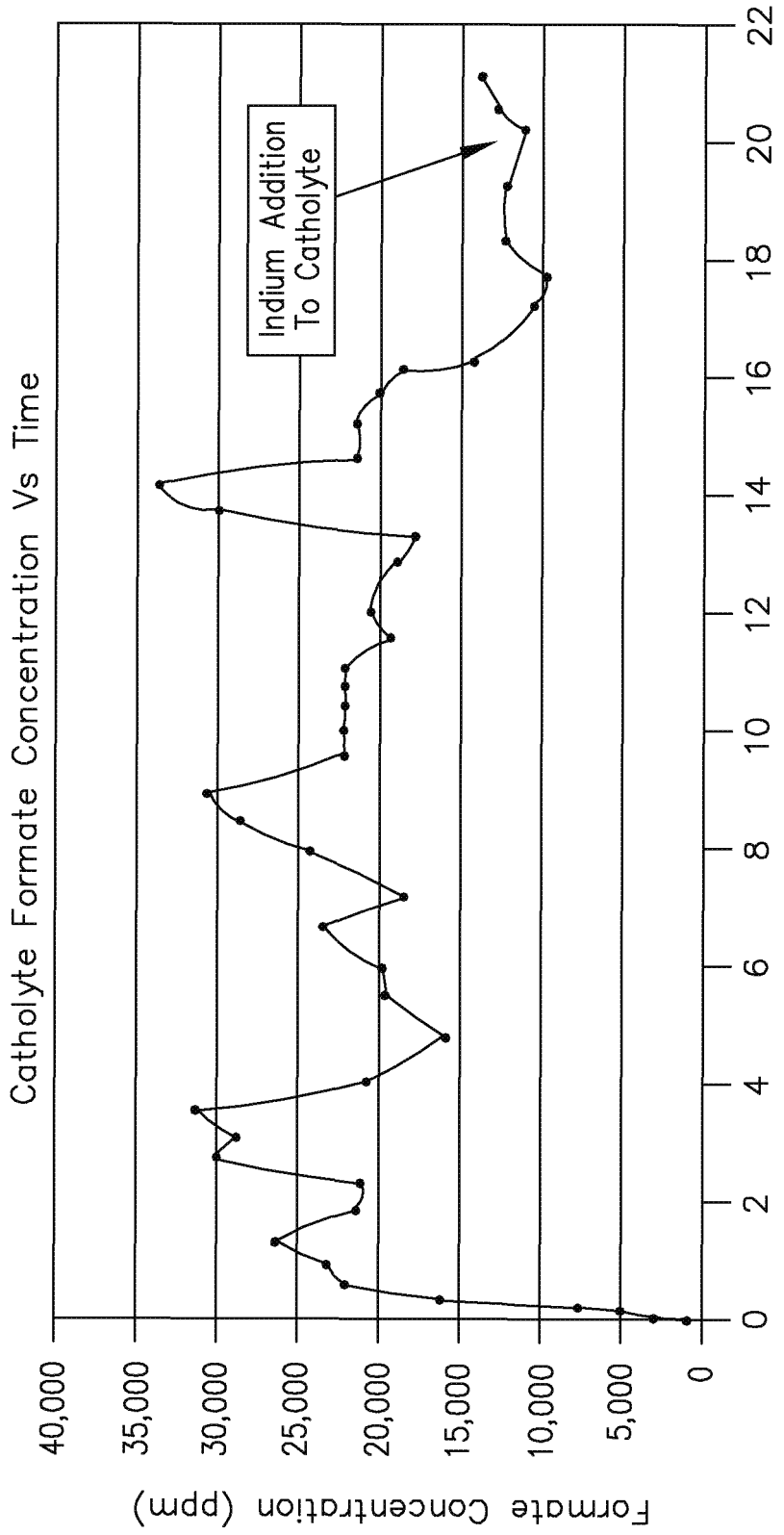

Catholyte Formate Concentration Vs Time
Indium Addition To Catholyte
Formate Concentration (ppm)
40,000
35,000
30,000
25,000
20,000
15,000
10,000
5,000
0
0
2
4
6
8
10
12
14
16
18
20
22
Time (Days)

FIG. 20

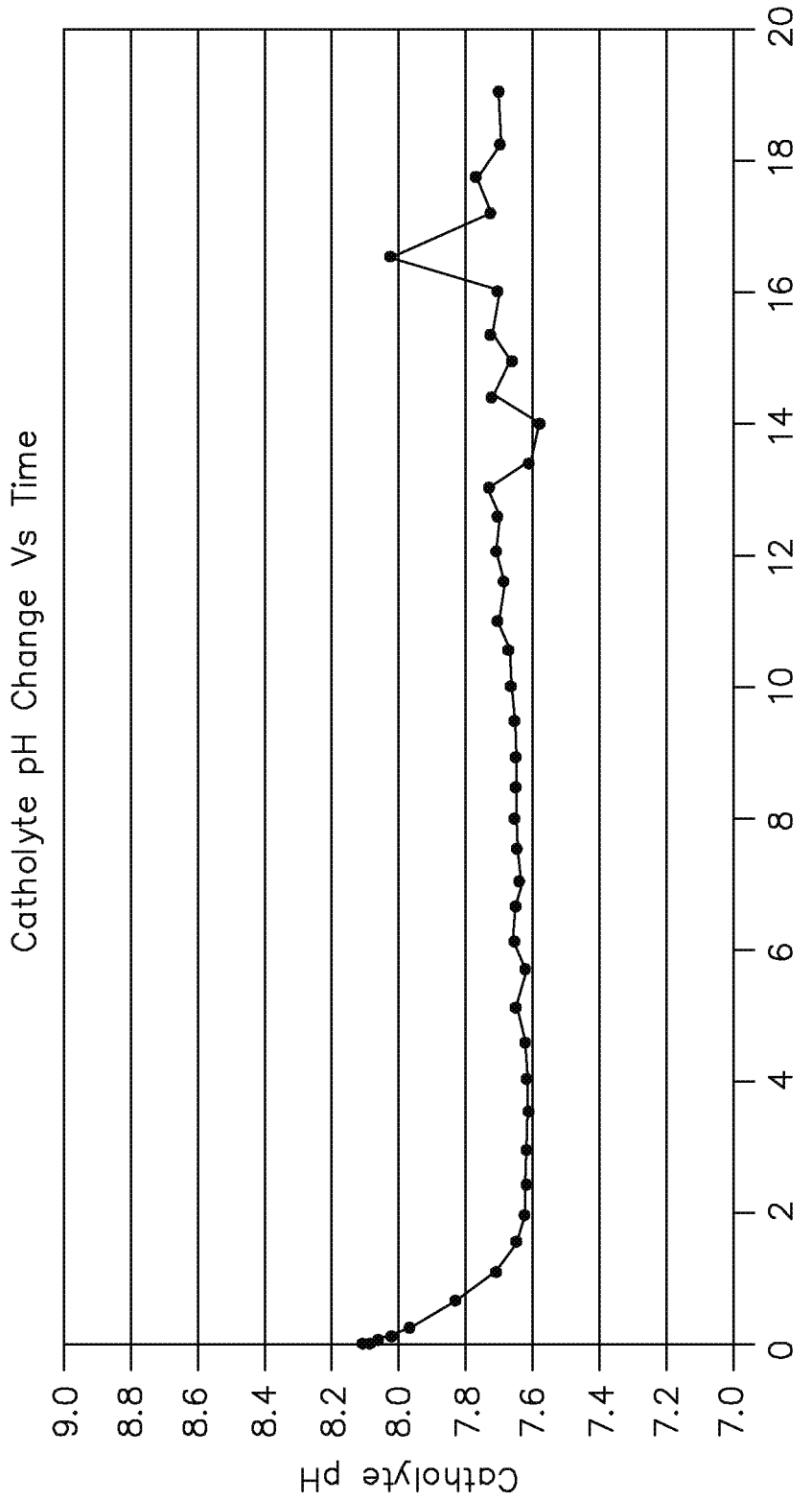

Catholyte pH Change Vs Time
Catholyte pH
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
0
2
4
6
8
10
12
14
16
18
20
Time (Days)

FIG. 21

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2007041872 A1 **[0004]**
- US 5290404 A **[0004]**
- US 4589963 A **[0004]**