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(54) Title: METHOD AND SYSTEM FOR ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE EMPLOYING A GAS DIFFUSION ANODE

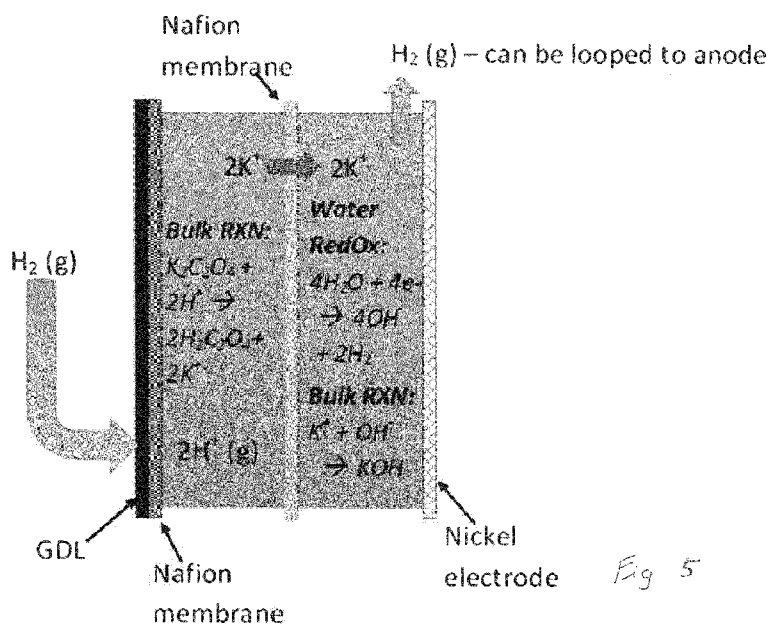


Fig 5

(57) Abstract: The invention relates to a method for the production of carboxylic acid based chemicals, such as carboxylic acids and salts, the method including: - receiving an anolyte feed at an anolyte region of an electrochemical cell including an anode, wherein the anode comprises or consists of a hydrogen depolarized gas diffusion anode; and - receiving a catholyte feed including carbon dioxide and an alkali metal bicarbonate at a catholyte region of the electrochemical cell including a cathode; and - applying an electrical potential between the anode and the cathode sufficient to reduce the carbon dioxide to at least one reduction product. and a system for the same. The invention further relates to a membrane-electrode assembly, comprising a metal gas diffusion electrode, hot pressed or coated with a, preferably hydrophobic, cation exchange membrane on one side.

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METHOD AND SYSTEM FOR ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE EMPLOYING A GAS  
DIFFUSION ANODE

## FIELD OF THE INVENTION

5 [0001] The present disclosure relates to methods and systems for the production of carboxylic acid based chemicals; a method for the production of oxalic acid and a specific gas diffusion electrode.

## BACKGROUND TO THE INVENTION

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

[0003] One implementation may be to convert carbon dioxide into economically valuable materials such as fuels and industrial chemicals. If the carbon dioxide may be converted using energy from renewable sources, it will be possible to both  
20 mitigate carbon dioxide emissions and to convert renewable energy into a chemical form that may be stored for later use. Electrochemical and photochemical pathways may be likely mechanisms for carbon dioxide conversion.

[0004] WO2015/184388 describes a method for reducing carbon dioxide comprising: receiving a feed of hydrogen gas at an anolyte region of an  
25 electrochemical cell including an anode, the anode including a gas diffusion electrode (GDE); receiving an anolyte feed at the anolyte region of the electrochemical cell; receiving a catholyte feed including carbon dioxide and an alkali metal bicarbonate at a catholyte region of the electrochemical cell including a cathode; applying an electrical potential between the anode and the cathode of  
30 the electrochemical cell sufficient to reduce the carbon dioxide to a reduction product, wherein the anolyte feed to the electrochemical cell includes water and a

hydrogen halide and wherein the reduction product is alkali metal formate. WO2015/184388 further describes that this alkali metal formate can be converted into an alkali metal oxalate via a thermal reaction and that the alkali metal oxalate can be converted to oxalic acid in an electrochemical acidification electrolyzer.

[0005] According to WO2015/184388 in the anode compartment, the electrochemical cell anode reaction may be the oxidation of hydrogen gas introduced into the anode GDE to form hydrogen ions ( $H^+$ ) or protons. In its figure 12, a schematic is shown illustrating an electrochemical cell utilizing a hydrogen GDE for the anode reaction.

[0006] Although good results are obtained with the method and/or system of WO2015/184388, there is still room for alternative processes and further improvement.

[0007] It would therefore be an advancement in the art to have a method, system and/or gas diffusion electrode with which similar, better, or economically more advantageous results can be achieved.

#### SUMMARY OF THE INVENTION

[0008] Such methods, systems and/or gas diffusion electrodes have been achieved with the methods, systems and gas diffusion electrodes according to the invention.

[0009] In a first embodiment the present invention provides a method including:

-receiving hydrogen gas at an anolyte region of an electrochemical cell or electrochemical acidification electrolyzer including an anode; and

-receiving an anolyte feed at the anolyte region of the electrochemical cell or electrochemical acidification electrolyzer; and

-receiving a catholyte feed including carbon dioxide and an alkali metal bicarbonate at the catholyte region of the electrochemical cell or electrochemical acidification electrolyzer including a cathode; and

-applying an electrochemical potential between the anode and the cathode, wherein the anode contains or consists of a membrane-electrode assembly formed by a platinum gas diffusion electrode hot pressed or coated with a hydrophobic

cation exchange material, wherein the hydrophobic cation exchange material preferably consists of a hydrophobic cation exchange membrane.

[0010] In a second embodiment the present invention provides a method for the production of carboxylic acid based chemicals, such as carboxylic acids and salts, the method including:

- receiving an anolyte feed at an anolyte region of an electrochemical cell including an anode, wherein the anode comprises or consists of a hydrogen gas diffusion anode; and

- receiving a catholyte feed including carbon dioxide and an alkali metal bicarbonate at a catholyte region of the electrochemical cell including a cathode; and

- applying an electrical potential between the anode and the cathode sufficient to reduce the carbon dioxide to at least one reduction product.

[0011] In a third embodiment the present invention provides a system for the production of carboxylic acid based chemicals, such as carboxylic acids and salts, the system including:

- an anolyte region positioned in an electrochemical cell or electrochemical acidification electrolyzer including an anode, which anolyte region is suitable for receiving an anolyte feed, wherein the anode comprises or consists of a hydrogen depolarized gas diffusion anode; and

- a catholyte region positioned in the electrochemical cell or electrochemical acidification electrolyzer including a cathode, which catholyte region is suitable for receiving a catholyte feed including carbon dioxide and an alkali metal bicarbonate; and

- means for applying an electrical potential between the anode and the cathode.

[0012] The methods and system are especially advantageous for the production of oxalic acid. In a fourth embodiment the present invention therefore also provides a method for the production of oxalic acid the method including:

- receiving an anolyte feed at an anolyte region of an electrochemical cell including an anode; and

- receiving a catholyte feed including carbon dioxide and an alkali metal bicarbonate at a catholyte region of the electrochemical cell including a cathode; and

- applying an electrical potential between the anode and the cathode sufficient to reduce the carbon dioxide to at least one reduction product; and
- converting the at least one reduction product and an alkali metal hydroxide to an alkali metal oxalate via a thermal reactor; and

- 5 - receiving the alkali metal oxalate at an electrochemical acidification electrolyzer; and
- converting the alkali metal oxalate to oxalic acid at the electrochemical acidification electrolyzer,

10 wherein a hydrogen depolarized gas diffusion anode is used for electrochemical acidification and/or the anode in the electrochemical cell and/or electrochemical acidification electrolyzer comprises or consists of a hydrogen depolarized gas diffusion anode. The electrochemical acidification electrolyzer and the electrochemical cell, may or may not be (part of) one and the same electrochemical cell.

15 In a fifth embodiment the present invention further provides a hydrogen depolarized gas diffusion anode for electrochemical acidification. Preferably the gas diffusion anode is a gas diffusion anode consisting of a membrane-electrode assembly formed by a platinum gas diffusion electrode hot pressed or coated with a hydrophobic cation exchange material, wherein the hydrophobic cation exchange

20 material preferably consists of a hydrophobic cation exchange membrane. As further explained below, the hydrogen depolarized gas diffusion anode may suitably also be a membrane-electrode assembly, comprising a metal gas diffusion electrode, hot pressed with a perfluorinated sulfonic acid based ion exchange membrane on one side.

25 [0013] Without wishing to be bound to any kind of theory it is believed that the use of a hydrogen depolarized gas diffusion anode, respectively the above mentioned membrane-electrode assembly, allows one to lower energy requirements, thus achieving an economically more advantageous result.

[0014] It is to be understood that both the foregoing general description and the

30 following detailed description are exemplary and explanatory only and are not necessarily restrictive of the present disclosure. The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate subject matter of the disclosure. Unless explicitly indicated otherwise, the

preferences for the different embodiments are interchangeable, that is, preferences applicable to one embodiment also apply to other embodiments. Together, the descriptions and the drawings serve to explain the principles of the disclosure.

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#### BRIEF DESCRIPTION OF THE DRAWINGS

[0015] 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:

10 Fig. 1 shows a system for production of oxalic acid starting with the electrochemical generation of carbon monoxide from carbon dioxide in accordance with an embodiment of the present disclosure;

15 Fig. 2 shows a system for production of oxalic acid starting with the electrochemical generation of formate using carbon dioxide in accordance with an embodiment of the present disclosure;

Fig. 3 shows a system for production of alkali metal formate using carbon dioxide in accordance with an embodiment of the present disclosure; and

20 Fig. 4 shows a schematic illustrating an electrochemical cell utilizing a hydrogen GDE for the anode reaction in producing oxalic acid from the reduction of carbon dioxide.

Fig. 5 shows a hydrogen depolarized gas diffusion anode for electrochemical acidification.

#### DETAILED DESCRIPTION OF THE INVENTION

25 [0016] Reference will now be made in detail to the subject matter disclosed, which is illustrated in the accompanying drawings.

[0017] The present disclosure describes a method and system for production of carboxylic based chemicals, including carboxylic acids and salts.

30 [0018] The method may employ an electrochemical cell reaction to produce carbon monoxide, CO, or alkali metal formate from a carbon dioxide feedstock. A thermal reaction with an alkali metal hydroxide catalyst may be used to combine, for example, two alkali metal formate molecules, into an alkali metal oxalate product.

[0019] The alkali metal oxalate may be then converted to oxalic acid by a membrane based electrochemical acidification process, where protons ( $H^+$  ions) formed at the anode may be used to replace the alkali metal ions, and the alkali metal ions ( $M^+$ ) may be captured as alkali metal hydroxide (MOH) at the cathode, and may be recycled to be used as the alkali metal hydroxide used in the intermolecular condensation process unit operation. The electrochemical acidification electrolyzers may comprise a combination of the use of electrodialysis (ED), including those ED electrolyzers employing bipolar membranes, sometimes called BPMED cells, as well as acidification cells utilizing cation membranes to efficiently optimize the conversion of the alkali metal oxalate to oxalic acid.

[0020] Before any embodiments of the disclosure are explained in detail, it is to be understood that the embodiments may not be limited in application per the details of the structure or the function as set forth in the following descriptions or illustrated in the figures. Different embodiments may be capable of being practiced or carried out in various ways. Also, it is to be understood that the phraseology and terminology used herein is for the purpose of description and should not be regarded as limiting. The use of terms such as "including," "comprising," or "having" and variations thereof herein are generally meant to encompass the item listed thereafter and equivalents thereof as well as additional items. Further, unless otherwise noted, technical terms may be used according to conventional usage. It is further contemplated that like reference numbers may describe similar components and the equivalents thereof.

[0021] Referring to Fig. 1, a system 100 for production of dicarboxylic acid, such as oxalic acid starting with the electrochemical generation of formate from the electrochemical reduction of carbon dioxide in accordance with an embodiment of the present disclosure is shown. System 100 may include an electrochemical cell 110. Electrochemical cell 110 (also referred as a container, electrolyzer, or cell) may be implemented as a divided cell. The divided cell may be a divided electrochemical cell and/or a divided photo-electrochemical cell. Electrochemical cell 110 may include an anolyte region and a catholyte region. Anolyte region and catholyte region may refer to a compartment, section, or generally enclosed

space, and the like without departing from the scope and intent of the present disclosure.

[0022] Catholyte region may include a cathode. Anolyte region may include an anode. An energy source (not shown) may generate an electrical potential between the anode and the cathode of electrochemical cell 110. The electrical potential may be a DC voltage. Energy source may be configured to supply a variable voltage or constant current to electrochemical cell 110. A separator may selectively control a flow of ions between the anolyte region and the catholyte region. Separator may include an ion conducting membrane or diaphragm material.

[0023] Electrochemical cell 110 may operate to perform an electrochemical reduction of carbon dioxide in an electrochemical cell producing carbon monoxide (CO) and hydrogen as cathode products and oxygen as an anode product when using an anolyte comprising sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). In an alternative embodiment, the anolyte comprising sulfuric acid may be replaced with an anolyte comprising a hydrogen halide, such as HBr.

[0024] The CO generated from electrochemical cell 110 may be separated from the hydrogen and then passed to a thermal reactor 120. Thermal reactor may react the carbon monoxide with an alkali metal hydroxide, such as KOH via a thermal intermolecular condensation reaction to form alkali metal formate. Thermal reactor 120 may operate to perform a thermal decomposition reaction or a carbonylation reaction, which may be reactions which incorporate CO into organic and inorganic chemical structures.

[0025] Alkali metal formate formed from thermal reactor 120 may be passed to another thermal reactor 130. Thermal reactor 130 may perform a second thermal intermolecular condensation reaction employing an alkali metal hydroxide (e.g. KOH) that may promote the reaction to produce alkali metal oxalate. While system 100 of Fig. 1 depicts a thermal reactor 120 and thermal reactor 130, it is contemplated that a single thermal reactor may be employed with system 100 without departing from the scope and intent of the present disclosure.

[0026] Alkali metal oxalate from thermal reactor 130 may be dissolved in water and may be passed to an electrochemical acidification electrolyzer 140.



Electrochemical acidification electrolyzer 140 may produce a dicarboxylic acid, such as oxalic acid. Electrochemical acidification electrolyzer 140 may be a membrane based unit including of at least three regions, including an anode region, one or more central ion exchange regions, and a cathode region. It is contemplated that an energy source (not shown) may generate an electrical potential between the anode and the cathode of electrochemical acidification electrolyzer 140 sufficient to produce oxalic acid. Alkali metal oxalate may be passed through the central ion exchange region where alkali metal ions may be replaced with protons, and the displaced alkali metal ions pass through the adjoining membrane into the cathode region to form MOH.

[0027] In line with one of the embodiments of the current invention, a hydrogen depolarized gas diffusion anode can be used for the electrochemical acidification. That is, the anode in electrochemical acidification electrolyzer can suitably comprise or consist of a hydrogen depolarized gas diffusion anode. Preferences are as indicated for such hydrogen depolarized gas diffusion anode below.

[0028] The dicarboxylic acid, such as an oxalic acid product may be purified to produce a final purified product, or may be further processed as a chemical intermediate to produce another product, such as monoethylene glycol, using a reduction process such as an electrochemical reduction or a catalytic hydrogenation.

[0029] Aqueous KOH from electrochemical acidification electrolyzer 140 may be passed to an evaporator 150. Evaporator 150 may evaporate the water from aqueous KOH product using steam or another heat source, converting it into a concentrated aqueous solution and/or solid with 5% or less water content as needed in electrochemical cell 110 and thermal reactor 120.

[0030] In an alternative embodiment, electrochemical cell 110 may utilize a hydrogen gas diffusion electrode for the anode reaction in producing oxalic acid from the reduction of carbon dioxide. The use of gas diffusion electrodes (GDE's) may be utilized in producing formate from the reduction of carbon dioxide. In the anode compartment, the electrochemical cell anode reaction may be the oxidation of hydrogen gas introduced into the anode GDE to form hydrogen ions ( $H^+$ ) or protons. These protons may then preferably pass through the adjoining cation ion exchange compartment or into an adjacent ion exchange compartment.

[0031] Figure 4 shows one of the hydrogen anode GDE configurations as system electrochemical cell drawing 1500 in a cross section view, not showing some of the internal gas passages within the anode current collector. The electrochemical cell may include an anode current collector containing an internal gas plenum with a multitude of micro-channels or grooves that connect to the hydrogen GDE, so that hydrogen gas may be evenly distributed and contact the GDE. The micro-channels may run horizontally or vertically. The hydrogen gas may preferably be introduced into the anode compartment from an upper entry port in the anode compartment and flow downwardly into the plenum as shown, and the depleted hydrogen may then exit at the bottom of the anode compartment. The hydrogen may be humidified with solvent vapor used in the anolyte compartment as needed. The anode current collector may be a carbon or graphite material or comprise metals if they are resistant to the anolyte electrolyte reactions and acidity that may be formed in the anolyte solution. The hydrogen may also be operated in a co-current or countercurrent flow configuration.

[0032] Adjacent to the right of the anode GDE may be an anode trickle bed solution distributor or percolator, where an anolyte solution may be introduced at a port at the top of the anode compartment such that the solution may be evenly distributed and the solution is distributed evenly down the length of the trickle bed distributor and exits the bottom of the anode compartment. The solution may be fed a specific flow rates, in the range of 0.001 to 10 liters per minute or more depending on the electrochemical cell dimensions, such that the anode GDE may not be completely flooded with the anolyte solution due to excessive pressure, and so as to maintain good ionic contact with the anode GDE for the transfer of protons into the anolyte solution. The flow and pressure of the anolyte flow should be such that minimal amounts of anolyte solution may pass through the GDE into the hydrogen gas plenum inside the anode current collector, and that the hydrogen gas oxidation within the GDE may be sufficient, so as to obtain a reasonable anode current density, in the range of 10 ma/cm<sup>2</sup> to 500 ma/cm<sup>2</sup>, or more preferably 50 ma/cm<sup>2</sup> to 200 ma/cm<sup>2</sup>. The anode trickle bed may comprise a thin construction, between about 0.1 cm to 10 cm in thickness, and preferably as thin as possible in the range of 0.2 to 5 cm in thickness to reduce any IR voltage drop to a minimum. The anode trickle bed may be made from non-conductive corrosion resistant

polymer plastics, such as PTFE, polypropylene, PVDF and the like, in the form of screen-like or convoluted forms so to distribute the solution evenly as it passes down the anode GDE structure. The entry and exit ports of the anolyte compartment are designed such that the flow distribution of anolyte liquid is uniform along the cross section of the trickle bed at the top and bottom. Alternatively, the trickle bed material may be comprised of conductive carbon and graphite, and may contain some of the hydrogen GDE catalyst on its surfaces. The GDE may be partially bonded to the separator or membrane for improved electrical conduction or contact.

5 [0033] The separator located between the anode and cathode compartments may be a membrane type, such as a cation membrane that may ionically conduct cations, such as  $H^+$  ions, through the membrane to the cathode compartment and may prevent or reduce the amount of back migration of anions from the catholyte compartment back into the anolyte compartment. Correspondingly, if the formate cell design may employ an intervening ion exchange compartment, the cation membrane may prevent the same back migration of anions from the adjoining cation membrane of the ion exchange compartment into the anolyte compartment. The selected cation membranes may preferably be stable to the solvent and salts in the electrochemical cell, such as the perfluorinated sulfonic acid membranes under the trade name of Nafion. The separator may also be, as discussed previously, a microporous separator, with fine pores in the 0.001 to 1 micron pore size range, such that it limits or controls solution or solvent bulk flow from the catholyte to the anolyte. The bulk flow may be controlled by the flow pressure of the catholyte solution flowing in the catholyte compartment.

15 25 [0034] The catholyte flow stream preferably enters the bottom of the catholyte compartment and exits from the top of the catholyte compartment in order to facilitate the removal of gases in the catholyte compartment. The catholyte flow rate may range from 0.01 to 10 liters/minute or more depending on the electrochemical cell dimensions and operating current density. The catholyte compartment utilizes a high surface area cathode structure for electrochemically reducing carbon dioxide in the catholyte to formate. The cathode materials that may be suitable are as described in this application. The operating pressure of the catholyte compartment may be in the range of 0.1 to 5 psig, or in the range of 1 to

30 psig or greater. The operating pressure may be a function of the catholyte flow rate and the flow resistance of the high surface area cathode structure employed.

[0035] The preferred solvent for the anolyte solution is an aqueous solution containing an electrolyte such as sulfuric acid or non-oxidizable acid to be a supporting electrolyte as needed. Organic solvents added to the anolyte in quantities of 50 wt% or less may be employed, such as methanol or ethanol, but may not be as preferred if they may interfere with the hydrogen oxidation at the anode. Salts that may be added to the anolyte electrolyte that may interfere with the GDE hydrogen oxidation are not preferred.

[0036] As an alternative embodiment, the electrochemical cell configuration may employ anode and cathode GDE structures that are in direct contact with a cation membrane separator.

[0037] In a further embodiment, ionically conductive materials, such as ion exchange materials such as resins or ionomers that are insoluble to the solvents may be used or placed between the anolyte and catholyte GDE's so as to provide a conductive ionic path for the ions to migrate. Alternatively, gel-type membranes that may comprise ion exchange structures that may hold ionic groups such as phosphoric acid in its structure and the like may be used. Membranes of these types that may be used are those used or proposed for use in phosphoric acid fuels and the like.

[0038] Referring to Fig. 2, a system 200 for production of dicarboxylic acid, such as oxalic acid, starting with the electrochemical generation of formate using carbon dioxide in accordance with an embodiment of the present disclosure is shown. System 200 may provide an alternative system for production of oxalic acid as produced by systems 100 of Fig. 1.

[0039] System 200 may include an electrochemical cell 210, for which preferences similar to electrochemical cell 110 would apply. Electrochemical cell 210 may operate to perform an electrochemical reduction of carbon dioxide with an alkali metal carbonate cathode feed, which may be formed from the reaction of CO<sub>2</sub> with MOH, to produce alkali metal formate directly. The alkali metal formate product solution concentration from the catholyte compartment of electrochemical cell 210 may range from 1 wt% to 30 wt% or more based on the formate ion, and preferably range from 5 wt% to 20 wt% as formate. The

corresponding % weight as the alkali metal formate, for example alkali metal formate may be based on the molecular weight of the alkali metal compound.

[0040] Alkali metal formate may be passed to a thermal reactor 220. Thermal reactor 220 may perform a thermal intermolecular condensation reaction with an  
5 alkali metal hydroxide (e.g., KOH) to produce alkali metal oxalate.

[0041] Alkali metal oxalate from thermal reactor 220 may be dissolved in water and may be passed to an electrochemical acidification electrolyzer 240. For Electrochemical acidification electrolyzer 240 similar or identical preferences and embodiments apply as for electrochemical acidification electrolyzer 140 illustrated  
10 in Figure 1. As for Figure 1, in line with one of the embodiments of the current invention, a hydrogen depolarized gas diffusion anode can be used for the electrochemical acidification in electrochemical acidification electrolyzer 240. That is, the anode in electrochemical acidification electrolyzer 240 can suitably comprise or consist of a hydrogen depolarized gas diffusion anode. Preferences are  
15 as described below for the hydrogen depolarized gas diffusion anode.

[0042] Similarly to Figure 1, the dicarboxylic acid, such as oxalic acid product may be purified to produce a final purified product, or may be further processed as a chemical intermediate to produce another product, such as monoethylene glycol, using an electrochemical reduction or thermochemical process.

[0043] Aqueous KOH from electrochemical acidification electrolyzer 240 may be  
20 passed to an evaporator 250. Evaporator 250 may evaporate the water from aqueous KOH product using steam or another heat source, converting it into a concentrated aqueous solution and/or solid with 5 wt% or less water content as needed in the electrochemical cell 210 or thermal reactor 220.

[0044] Again, as for Figure 1, in an alternative embodiment, electrochemical cell  
25 210 may utilize a hydrogen gas diffusion electrode for the anode reaction. Preferences are as described above for electrochemical cell 110.

[0045] Referring to Fig. 3, a system 300 for production of a formate, such as alkali metal formate, using carbon dioxide in accordance with an embodiment of the  
30 present disclosure is shown. Figure 3 illustrates the electrochemical reduction of carbon dioxide in the production of an alkali metal formate as shown in electrochemical cell 210 of Fig. 2. Electrochemical cell 310 may include an anolyte input feed 310 and a catholyte input feed 312 to produce a product 314.

Product 314 may be a solution of alkali metal formate with an excess alkali metal bicarbonate ( $\text{KHCO}_3$ ). Anolyte region 320 may have a titanium anode 322 having an anode electrode catalyst coating facing cation exchange membrane 330. Anode mesh screen 332 may be a folded expanded titanium screen with an anode electrocatalyst coating and provides spacing and contact pressure between anode 322 and cation exchange membrane 332. Cation exchange membrane 330 may selectively control a flow of ions between anolyte region 320 from catholyte region 340.

[0046] Catholyte region 340 may have a mounted cathode 342, which may be a metal electrode with an active electrocatalyst layer on the front side facing membrane 330. High surface area cathode structure 344 may be mounted with direct contact pressure between the face of cathode 342 and cation membrane 330.

[0047] As shown in Fig. 1 and Fig. 2, feeding anolyte region 320 may be stream 310 which may include anolyte, the anolyte comprising an aqueous sulfuric acid electrolyte solution. Stream 310 may enter the anolyte region 320 and flow by the face of anode 322 through folded anode screen 332. Anode reactions may comprise splitting water into oxygen ( $\text{O}_2$ ) and hydrogen ions ( $\text{H}^+$ ) or protons. The gases and liquid mixture from anolyte region 320 may leave as stream 350, which flows by temperature sensor 352 monitoring a solution temperature in the stream, and into anolyte gas/liquid disengager 354. In disengager 354, the gas may be vented as stream 356, and excess anolyte overflow leaves as stream 358. Stream 360 may be a gas-depleted exit stream from the anolyte disengager 354, with a deionized water feed stream 362 and a sulfuric acid make-up feed stream 364 added to the recirculation stream to maintain anolyte acid strength and volume. Stream 360 with added streams 362 and 364 may then pass through an optional heat exchanger 370 with a cooling water supply 372, and then becomes stream 310 feeding into the anolyte region 320.

[0048] Electrochemical cell 310 may include a catholyte region 340 which includes cathode 342 having an electrocatalyst surface facing membrane 330. High surface area cathode structure 344 may be mounted between membrane 330 and cathode 342, relying on contact pressure with cathode 342 for conducting electrical current into the structure. The interface between high surface area structure 344 and

membrane 330 may utilize a thin expanded plastic mesh insulator screen (not shown) to minimize direct contact with the high surface area cathode material with the membrane 330.

5 [0049] Feed stream 312 may feed into catholyte region 340, flowing through the high surface area structure 344 and across the face of cathode 342 where cathode reduction reactions between carbon dioxide, electrolyte, and cathode material at the applied current and voltage potential produce exit stream 314, the exit stream including a formate.

10 [0050] Stream 314 may be the exit solution and gas mixture product from the cathode reaction which flows by pH monitoring sensor 374 and temperature sensor 352 and then into catholyte gas/liquid disengager 380 where the gas exits as stream 382 and formate/electrolyte overflow exits as stream 384, and the gas-depleted stream leaves the disengager as stream 386. Stream 386 may then enter an input of catholyte recirculation pump 390, which then passes through heat  
15 exchanger 392 which uses cooling water 372, then passes by temperature sensor 352. A fresh catholyte electrolyte feed 394 may be metered into stream 386 which may be used to adjust the catholyte flow stream pH into the catholyte region 340 and control a product overflow rate and sets the formate product concentration, with the pH monitored by pH sensor 374. Carbon dioxide flow stream 396 may be  
20 metered into the flow stream which enters the catholyte region 340 as stream 312.

[0051] The following present various exemplary combinations of cell configurations, electrode structures, and anolyte/catholyte compositions that may be used in the electrochemical CO and/or formate, and electrochemical acidification (EA) electrolyzers in the above described processes.

25 [0052] The cathode of the electrochemical cell 110, 210 and 310 and electrochemical acidification electrolyzer 140 may be a high surface area electrode. The void volume for the cathode may be from about 30% to 98%. The surface area of the cathode may be from  $2 \text{ cm}^2/\text{cm}^3$  to  $2,000 \text{ cm}^2/\text{cm}^3$  or higher. The surface areas may be further defined as a total area in comparison to the  
30 current distributor/conductor back plate area with a preferred range of from 2 to 1000 times the current distributor/conductor back plate area.

[0053] The cathode of the electrochemical cell 110, 210 and 310 may be electrolessly plated indium or tin on a copper woven mesh, screen or fiber

structure. Indium-copper intermetallics may be formed on the copper woven mesh, screen or fiber structure. The intermetallics may be harder than the soft indium metal, and allow better mechanical properties in addition to usable catalytic properties. The indium electrocatalyst coating may also be prepared by electroplating indium onto a suitable corrosion resistant metal substrate, such as a tin plated copper or tin plated stainless steel metal high surface area substrate. Alternatively, the indium may be plated onto a high surface area carbon substrate, such as a carbon felt or cloth composed of fibers, which may already have an applied tin-based coating. Also, the indium electrocatalyst may be applied by co-electroplating a mixture of indium with another metal, such as Sn, Zn, Bi, or Pb, onto a suitably prepared coated metal or carbon substrate, such that the coating is physically and chemically compatible with the applied indium/co-metal electroplated external layer. Suitable indium-based electrocatalytic coatings are corrosion resistant to the catholyte solutions, salts, and operating pH of the catholyte.

[0054] In the electrochemical reduction of carbon dioxide metals including Pb, Sn, Hg, Tl, In, Bi, Zn, and Cd among others may produce formic acid (or formate) as a major C<sub>1</sub> product in aqueous solutions. Alloy combinations of these metals such as Hg-Cu, Sn-Cd, Sn-Zn, Cu-Sn, may form at various performance efficiencies. Precious metals, such as Pd, Au, Ru, Ir and Ag may also be included in small amounts in the alloys which may improve the reduction of CO<sub>2</sub> to formate. One of the issues may be that a number of these metals, such as Sn and Cu, may be that the surface changes and deactivates or loses the Faradaic conversion activity in producing formate. The surface then may have to be reactivated by a reverse current or polarity. In the production for formation of C<sub>2+</sub> chemicals, such as oxalic acid and glycolic acid, metals such as Ti, Nb, Cr, Mo, Ag, Cd, Hg, Tl, As, and Pb as well as their alloys or mixtures as well as Cr-Ni-Mo steel alloys among many others may result in the formation of these higher C<sub>2+</sub> products.

[0055] In another embodiment, the cathode surfaces may be renewed by the periodic addition of indium salts or a mix of indium/tin salts in situ during the electrochemical cell operation. Electrochemical cell 110, 210 or 310 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.

[0056] In another exemplary embodiment, in preparing cathode materials for the production of  $C_{2+}$  chemicals, the addition of metal salts that may reduce on the surfaces of the cathode structure may be also used, such as the addition of Ag, Au, Mo, Cd, Sn, etc. to provide a catalytic surface that may be difficult to prepare directly during cathode fabrication or for renewal of the catalytic surfaces.

[0057] In another exemplary embodiment, Magneli phase titanium oxides, in particular  $Ti_4O_7$  may be used as a cathode base material, which may also be impregnated or coated with one or more of the aforementioned suitable cathode metals, which may include Ag, Au, In, Mo, Cd, Sn, Cu, Hg, Tl, Bi, Ti, Nb, Zr, As, Cr, Co, Zn, Pb, and their alloys and combinations. These Magneli phase materials may be in the form of three dimensional porous materials in the shape of plates, foams, pellets, powders, and the like. One manufacturer, Atraverda, Ltd., manufactures these under the trade name of Ebonex.

[0058] The cathode may include stainless steels and nickel electrodes. Cathode 412 may include coatings on the cathode to reduce the hydrogen overpotential.

[0059] An alkali metal hydroxide range for the electrochemical acidification electrolyzer 140 may be 5% to 50% by weight, and more preferably 10% to 45% by weight. The alkali metal hydroxide examples may be NaOH, KOH, CsOH and the like.

[0060] Cathode materials for the cathode of electrochemical cell 110, 210 and 310, for carbon monoxide production from  $CO_2$  may include precious and noble metals, Cu, Ag, Au, and their oxides, specifically the oxides of copper. Other d-block metals, such as Zn and Ni, may be selective for CO reduction in aqueous media. Regardless of specificity for CO as a  $CO_2$  reduction product, a cathode for electrochemical cell 110, 210 and 310 for an aqueous system for  $CO_2$  reduction to CO may have a high hydrogen overpotential to prevent competing  $H_2$  formation.

[0061] Anions used for CO production at the cathode may be any species stable at working potentials such as sulfate, chloride or bicarbonate.  $CO_2$  reduction to CO may favor high pH due to limited competing  $H_2$  formation; however there may be a practical pH maximum at around 8.5 for a saturated  $CO_2$  solution due to the

formation of carbonic acid on dissolution. There may be no strict lower limit that may have been observed. Depending on the chemistry of the system, the pH of the catholyte region of electrochemical cell 110, 210 and 310 may range from 3 to 12. The pH may be a function of the catalysts used, such that there may be no corrosion at the electrochemical cell 110, 210 and 310 and catholyte operating conditions.

[0062] Electrolytes for the electrochemical cell 110, 210 and 310 for forming CO and formates may include alkali metal bicarbonates, carbonates, sulfates, and phosphates, borates, ammonium, hydroxides, chlorides, bromides, and other organic and inorganic salts. The electrolytes may also include non-aqueous electrolytes, such as propylene carbonate, methanesulfonic acid, methanol, and other ionic conducting liquids, 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.

[0063] The electrochemical cell catholyte solution may also comprise an aqueous or non-aqueous based solution. The solution may contain an organic solvent, for example methanol or ethanol, that may help provide a higher solubility of carbon dioxide in the solution over that of aqueous solutions. The organic solvent may be fully soluble in the aqueous catholyte solution or may also be present as an emulsion in the catholyte solution. The solvent may be a polar or aprotic type solvent. Solvents may include carbonates, such as propylene carbonate, acetone, alcohols - including primary, secondary, and tertiary types, dimethyl sulfoxide, dioxane, aromatic hydrocarbons such as toluene and cyclohexane, chlorinated as well as fluorinated solvents such as chloroform, aprotic solvents such as acetonitrile, and the like. An aqueous solvent in this disclosure is defined as a solution containing less than 50 wt% of organics in comparison to the water content. The organics may be chosen in regards to improving carbon dioxide solubility in the solution, as a moderator of the catholyte salt solubility such as formate, and in improving or enabling the cathode chemistry in the formation of C<sub>2</sub><sup>+</sup> compounds, which may be promoted by the use of the organics which exclude water in the cathode reaction. Examples of a C<sub>2</sub><sup>+</sup> carbon dioxide reduction

products are oxalate, glycolate, and glyoxylates. Other carbon dioxide products may include acetic acid, ethanol, methanol, as well as others.

[0064] Electrolytes for the anolyte region of the electrochemical cell 110, 210 and 310 may include: alkali metal hydroxides, (e.g. as KOH, NaOH, LiOH) in addition to ammonium hydroxide; inorganic acids such as sulfuric, phosphoric, and the like; organic acids such as methanesulfonic acid in both non-aqueous and aqueous solutions; and alkali halide salts, such as the chlorides, bromides, and iodine salts such as NaF, NaCl, NaBr, LiBr, KF, KCl, KBr, KI, and NaI, as well as their hydrogen halide forms, such as HCl, HF, HI, and HBr. The alkali halide salts may produce, for example, fluorine, chlorine, bromine, or iodine as halide gas or dissolved aqueous products from the anolyte region. Methanol or other hydrocarbon non-aqueous liquids may also be used, and they 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, using HBr as the anolyte, with the formation of bromine at the anode, which require a significantly lower anode voltage potential than chlorine formation. Hydriodic acid, HI, may form iodine at anode potential voltages even lower than that of bromine.

[0065] 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 hydrogen halides such as HCl, HBr and HI. The hydrogen 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 may 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 hydrogen halide byproduct from the reaction may be recycled back to the electrochemical cell anolyte.

[0066] Catholyte cross sectional area flow rates may range from 2 to 3,000 gpm/ft<sup>2</sup> or more (0.0076 - 11.36 m<sup>3</sup>/m<sup>2</sup>). Flow velocities may range from 0.002 to 20 ft/sec (0.0006 to 6.1 m/sec).

[0067] Catholyte region of the electrochemical cell 110, 210 and 310 may include at least one catalyst. The catalyst may be a homogeneous heterocyclic catalyst which may be utilized in the catholyte region to improve the Faradaic yield to formate. Homogeneous heterocyclic catalysts may include, for example, one or more of pyridine, tin 2-picoline, 4-hydroxy pyridine, adenine, a heterocyclic amine containing sulfur, a heterocyclic amine containing oxygen, an azole, a benzimidazole, a bipyridine, a furan, an imidazole, an imidazole related species with at least one five-member ring, an indole, a lutidine, methylimidazole, an oxazole, a phenanthroline, a pterin, a pteridine, pyridine, a pyridine related species with at least one six-member ring, a pyrrole, a quinoline, or a thiazole, and mixtures thereof.

[0068] Operating electrochemical cell 110, 210 and 310 at a higher operating pressure in the catholyte region may allow more dissolved CO<sub>2</sub> to dissolve in the aqueous electrolyte. Typically, 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 electrochemical cell 110, 210 and 310 anolyte may also be operated in the same pressure range to minimize the pressure differential on the membrane separating the two electrode regions. Special electrochemical designs may be required to operate electrochemical units at higher operating pressures up to about 60 to 100 atmospheres or greater, which may be in the liquid CO<sub>2</sub> and supercritical CO<sub>2</sub> operating range.

[0069] In another embodiment, a portion of the catholyte recycle stream may be separately pressurized using a flow restriction with back pressure or using a pump with CO<sub>2</sub> injection such that the pressurized stream may be then injected into

the catholyte region of the electrochemical cell 110, 210 and 310, and potentially increasing the amount of dissolved CO<sub>2</sub> in the aqueous solution to improve the conversion yield.

[0070] Catholyte region and anolyte region of electrochemical cell 110, 210 and 5 310 may have operating temperatures that may range from -10 to 95 °C, more preferably 5 - 60°C. The lower temperature may be limited by the electrolytes used and their freezing points. In general, the lower the temperature, the higher the solubility of CO<sub>2</sub> in the aqueous solution phase of the electrolyte which may result in obtaining higher conversion and current efficiencies. However, operating 10 electrochemical cell voltages may be higher, such that an optimization may be required to produce the chemicals at the lowest operating cost. In addition, the operating temperatures of the anolyte and catholyte may be different, whereby the anolyte is operated at a higher temperature and the catholyte is operated at a lower temperature.

[0071] The electrochemical cell 110, 210 and 310 and the electrochemical 15 acidification (EA) electrolyzer 140 may be zero gap, flow-through electrolyzers with a recirculating catholyte electrolyte with various high surface area cathode materials. For example, flooded co-current packed and trickle bed designs with various high surface area cathode materials may be employed. The stack cell 20 design may be bipolar and/or monopolar.

[0072] The anode of the electrochemical cell 110, 210 and 310 and the EA 25 electrolyzer 140 may include one or more anode coatings. For example, for acid anolytes and oxidizing water under acid conditions, electrocatalytic coatings may include: precious metal and precious metal oxides such as ruthenium and iridium oxides, as well as platinum and gold and their combinations as metals and oxides 30 on valve metal conductive substrates such as titanium, tantalum, or niobium as typically used in the chlor alkali industry or other electrochemical processes where they may be stable as anodes. Magneli phase titanium oxides, in particular Ti<sub>4</sub>O<sub>7</sub> may be used as an anode material, which may also be impregnated or coated with the aforementioned precious metals and precious metal oxides. These magneli phase materials may be in the form of three dimensional porous materials in the shape of plates, foams, pellets, powders, and the like. One manufacturer, Atraverda, Ltd., manufactures these under the tradename of Ebonex. For other

anolytes such as alkaline or hydroxide electrolytes, the electrocatalytic coatings may include carbon, graphite, cobalt oxides, nickel, stainless steels, and their alloys and combinations which may be stable as anodes under these alkaline conditions.

5 [0073] Membrane 330 may be cation ion exchange type membranes such as those having a high rejection efficiency to anions. For example perfluorinated sulfonic acid based ion exchange membranes such as DuPont Nafion<sup>®</sup> 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  
10 the supplier trade names such as Flemion<sup>®</sup>. Other multi-layer perfluorinated ion exchange membranes used in the chlor alkali industry and having a bilayer construction of a sulfonic acid based membrane layer bonded to a carboxylic acid based membrane layer may be employed to efficiently operate with an anolyte and catholyte above a pH of about 2 or higher. These membranes may have a higher  
15 anion rejection efficiency. These may be sold by DuPont under their Nafion<sup>®</sup> 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 may be made from of various cation ion exchange materials may also be used if the anion rejection may be not as critical,  
20 such as those sold by Sybron under their trade name Ionac<sup>®</sup>, AGC Engineering (Asahi Glass) under their Selemion<sup>®</sup> trade name, and Tokuyama Soda among others.

[0074] Various alkali metal hydroxides may be employed at the electrochemical cell 110, 210 and 310 and/or a thermal reactors. For example, hydroxides of  
25 lithium, sodium, potassium, and rubidium, and cesium may be used. Further, alkaline earth metal hydroxides may also be used.

[0075] The thermal reactors may perform thermal intermolecular condensation reactions using alkali metal hydroxides as catalysts. Such condensation reactions may include chemical reactions in which two molecules or moieties (functional  
30 groups) combine to form one single molecule, together with the loss of a small molecule. When two separate molecules may be reacted, the condensation may be termed intermolecular. Since the reaction occurs at elevated temperatures, the reactions may be characterized as “thermal intermolecular condensation step”. If

water may be lost, the reactions may be characterized as “thermal intermolecular dehydration step”. These reactions may occur in an aqueous solution phase, such as with the reaction of CO with the alkali metal hydroxide, or as a melt of the alkali metal carboxylic acid and the alkali metal hydroxide in the thermal reaction.

5 [0076] Thermal reactors 120, 130 may operate at about 40 to 500°C, and more preferably at about 50 - 450°C. The operating temperatures may depend on the decomposition temperatures of the carboxylic acid and the optimum temperature to get the highest yields of the carboxylic product. A residence time of the reaction at optimum reaction temperatures may range from 5 seconds to hours,  
10 and the equipment chosen to conduct the reaction may be designed to provide the rate of heating and cooling required to obtain optimal conversion yields. This may include the use of cold rotating metal that may rapidly chill the hot thermal product after the thermal reaction period may be completed.

[0077] Thermal reactors 120, 130 may operate in air or an enriched oxygen  
15 atmospheres, as well as inert gas atmospheres, such as nitrogen, argon, and helium. Carbon dioxide and hydrogen atmospheres may also be employed to obtain the highest yield in the reaction, as well as partial CO atmospheres. Thermal reactors 120, 130 may be operated under a full or partial vacuum.

[0078] The use of CO from other sources, such as from the production of syngas  
20 from methane or natural gas reforming may be employed. CO may also come from other sources, such as process waste streams, where may be it separated from carbon dioxide.

[0079] Alkali metal hydroxide concentration ranges may be 2% to 99%, more preferably 5 to 98% by weight. The alkali hydroxide may run in molar excess of the  
25 alkali metal carboxylic acid being thermally processed in the initial reaction mix or in a continuous process where they may be mixed together. The anticipated molar ratios of the alkali metal carboxylic acid to alkali metal hydroxide may range from 0.005 to 100, and more preferably 0.01 to 50. It may be preferable to use the least amount of alkali metal hydroxide as possible for the reaction to reduce the  
30 consumption of the hydroxide in the process.

[0080] The process operating equipment that may be employed for thermal reactors 120, 130 may include various commercially available types. For the CO reaction with alkali metal hydroxide, the equipment that may be used may be

batch operation equipment, where gas may be injected into a solution mix of the alkali hydroxide. This may also be done in a continuous manner where there may be a feed input of fresh alkali metal hydroxide into a continuous stirred tank reactor (CSTR) with a CO feed into the solution through a gas diffuser into the solution. Alternatively, counter-current packed towers may be used where CO may be injected into the tower counter-current to the flow of alkali metal hydroxide.

[0081] For a alkali metal oxalate operation, thermal reactors 120, 130 may include equipment such as rotary kilns, and single pass plug flow reactors that may be used if the process required the thermal processing of a mixture of alkali metal formate and alkali hydroxide as a solid or hot melt mix. Preferably, the equipment would be operated in a continuous fashion, providing the required residence time for the reaction to go to completion at the selected temperatures, which may be followed by a cooling section.

[0082] A thermal intermolecular condensation process may also be conducted to produce higher carbon content carboxylic acids as well as converting the carboxylic acids into esters, amides, acid chlorides, and alcohols. In addition, the carboxylic acid products may be converted to the corresponding halide compounds using bromine, chlorine, and iodine.

[0083] Catalysts for the thermal conversion of the alkali metal formate may consist of various bases, including alkali metal hydroxide as well as other compounds that are bases. In addition, alkali metal and other hydrides may be used, since they also act as bases. Any other suitable catalysts that may be compatible with the formates in the calcination and provide high conversion yields are suitable for the process.

[0084] It is contemplated that method for production of dicarboxylic acid, such as oxalic acid, may include various steps performed by systems 100, 105, 200 and 205.

As indicated above, the hydrogen depolarized gas diffusion anode for electrochemical acidification may suitable comprise or consist of a membrane-electrode assembly. The membrane-electrode assembly preferably comprises a metal gas diffusion electrode, attached, hot pressed or coated with a, preferably



hydrophobic, cation exchange material on one side. The, preferably hydrophobic, cation exchange material is preferably a cation exchange membrane. More preferably the membrane-electrode assembly comprises a metal gas diffusion electrode, hot pressed or coated with a, preferably hydrophobic, cation exchange  
5 membrane on one side.

The hydrogen depolarized gas diffusion electrode or anode, respectively membrane-electrode assembly, suitably contains or consists of a metal capable of oxidizing hydrogen to hydrogen cations, preferably the metal is platinum.

Most preferably the metal gas diffusion electrode is a platinum gas diffusion  
10 electrode.

The, preferably hydrophobic, cation exchange material, respectively cation exchange membrane, is preferably a polytetrafluoroethylene (PTFE) based cation exchange membrane or a sulfonated polytetrafluoroethylene based cation exchange membrane. Materials that can be used include for example  
15 perfluorinated sulfonic acid based ion exchange membranes such as DuPont Nafion<sup>®</sup> 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<sup>®</sup>.

Without wishing to be bound by any kind of theory it is believed that the above  
20 described hydrogen depolarized gas diffusion electrode or anode, respectively membrane-electrode assembly, allows for the passage of hydrogen cations (protons) into the anolyte, whilst blocking the access of water to the electrode. Without wishing to be bound by any kind of theory it is further believed that advantageously less water is converted at the electrode, respectively assembly,  
25 resulting in a reduced need for polarization and reduced energy-consumption.

Referring to Figure 5, a hydrogen depolarized gas diffusion anode for electrochemical acidification is shown.

[0085] Hydrogen may be fed to a platinum gas diffusion electrode, hot pressed  
30 with a Nafion type membrane on one side forming a membrane-electrode assembly. The assembly will produce hydrogen cations. Oxalic acid (4-10%wt) may be made from potassium oxalate, or other oxalate salt, by employing the hydrogen ions to neutralize the oxalate in the bulk anolyte in the anode compartment. A

membrane comprising Nafion, or another membrane or combination of membranes that supports the transport of cations, will separate the anode and cathode compartments. Potassium hydroxide (20-45%wt) may be produced in the cathode compartment employing a cathode. Other hydroxides, such as sodium hydroxide, lithium hydroxide, and other hydroxides compatible with chlor-alkali electrochemical cells may be produced. Suitable cathode materials include nickel, palladium, rhodium, indium, cobalt, stainless steel, Inconel, and carbon nanotubes. Cathode materials may comprise any material suitable for use in a chlor-alkali electrochemical cell.

10 [0086] Hydrogen from the cathode may be recycled back to the anode.

[0087] The electrochemical cell or electrochemical acidification electrolyzer may preferably be operated at an electrical current density in the range from 3 to 4 kA/m<sup>2</sup> (kiloampère per square meter).

15 [0088] The electrochemical cell or electrochemical acidification electrolyzer may preferably be operated at a temperature in the range from 70 to 80°C (degrees Celsius).

[0089] It may be believed that the present disclosure and many of its attendant advantages will be understood by the foregoing description, and it will be apparent that various changes may be made in the form, construction and arrangement of the components without departing from the disclosed subject matter or without sacrificing all of its material advantages. The form described may be merely explanatory.

25

## CLAIMS

1. A method including:
- 5 -receiving hydrogen gas at an anolyte region of an electrochemical cell or electrochemical acidification electrolyzer including an anode; and
  - receiving an anolyte feed at the anolyte region of the electrochemical cell or electrochemical acidification electrolyzer; and
  - 10 -receiving a catholyte feed including carbon dioxide and an alkali metal bicarbonate at the catholyte region of the electrochemical cell or electrochemical acidification electrolyzer including a cathode; and
  - applying an electrochemical potential between the anode and the cathode, wherein the anode contains or consists of a membrane-electrode assembly formed by a platinum gas diffusion electrode hot pressed or coated with a hydrophobic cation exchange material, wherein the hydrophobic cation exchange material
  - 15 preferably consists of a hydrophobic cation exchange membrane.
2. A method for the production of carboxylic acid based chemicals, such as carboxylic acids and salts, the method including:
- 20 - receiving an anolyte feed at an anolyte region of an electrochemical cell including an anode, wherein the anode comprises or consists of a hydrogen depolarized gas diffusion anode; and
  - receiving a catholyte feed including carbon dioxide and an alkali metal bicarbonate at a catholyte region of the electrochemical cell including a cathode; and
  - 25 - applying an electrical potential between the anode and the cathode sufficient to reduce the carbon dioxide to at least one reduction product.
3. The method according to claim 2, wherein the hydrogen depolarized gas diffusion anode is a membrane-electrode assembly, comprising a metal gas
- 30 diffusion electrode, hot pressed or coated with a, preferably hydrophobic, cation exchange membrane on one side.

4. The method according to claim 3, wherein the membrane-electrode assembly comprises a platinum gas diffusion electrode, hot pressed or coated on one side with a polytetrafluoroethylene (PTFE) based cation exchange membrane or a sulfonated polytetrafluoroethylene based ion exchange membrane.

5

5. The method according to anyone of claims 2 to 4, wherein the cathode comprises or consists of nickel, palladium, rhodium, indium, cobalt, stainless steel or carbon.

10 6. A system for the production of carboxylic acid based chemicals, such as carboxylic acids and salts, the system including:

- an anolyte region positioned in an electrochemical cell or electrochemical electrolyzer including an anode, which anolyte region is suitable for receiving an anolyte feed, wherein the anode comprises or consists of a hydrogen depolarized gas diffusion anode; and
- 15 - a catholyte region positioned in the electrochemical cell including a cathode, which catholyte region is suitable for receiving a catholyte feed including carbon dioxide and an alkali metal bicarbonate; and
- means for applying an electrical potential between the anode and the cathode.

20

7. The method according to claim 6, wherein the hydrogen depolarized gas diffusion anode is a membrane-electrode assembly, comprising a metal gas diffusion electrode, hot pressed or coated with a, preferably hydrophobic, cation exchange membrane on one side.

25

8. The method according to claim 7, wherein the membrane-electrode assembly comprises a platinum gas diffusion electrode, hot pressed or coated on one side with a polytetrafluoroethylene (PTFE) based cation exchange membrane or a sulfonated polytetrafluoroethylene based ion exchange membrane.

30

9. The method according to anyone of claims 6 to 8, wherein the cathode comprises or consists of nickel, palladium, rhodium, indium, cobalt, stainless steel or carbon.

10. A method for the production of oxalic acid the method including:
- receiving an anolyte feed at an anolyte region of an electrochemical cell including an anode; and
  - 5 - receiving a catholyte feed including carbon dioxide and an alkali metal bicarbonate at a catholyte region of the electrochemical cell including a cathode; and
  - applying an electrical potential between the anode and the cathode sufficient to reduce the carbon dioxide to at least one reduction product; and
  - 10 - converting the at least one reduction product and an alkali metal hydroxide to an alkali metal oxalate via a thermal reactor; and
  - receiving the alkali metal oxalate at an electrochemical acidification electrolyzer; and
  - converting the alkali metal oxalate to oxalic acid at the electrochemical
  - 15 acidification electrolyzer,
- wherein a hydrogen depolarized gas diffusion anode is used for electrochemical acidification and/or the anode in the electrochemical cell and/or electrochemical acidification electrolyzer comprises or consists of a hydrogen depolarized gas diffusion anode.
- 20
11. The method according to claim 10, wherein the alkali metal is potassium or sodium.
12. The method according to anyone of claims 10 and 11, wherein the
- 25 electrochemical cell or electrochemical acidification electrolyzer is operated at an electrical current density in the range from 3 to 4 kA/m<sup>2</sup>.
13. The method according to anyone of claims 10 and 12, wherein the electrochemical cell or electrochemical acidification electrolyzer is operated at a
- 30 temperature in the range from 70 to 80°C.
14. The method according to anyone of claims 10 and 13, wherein the hydrogen depolarized gas diffusion anode is a membrane-electrode assembly, comprising a

metal gas diffusion electrode, hot pressed or coated with a, preferably hydrophobic, cation exchange membrane on one side.

5 15. The method according to anyone of claims 10 and 14, wherein the membrane-electrode assembly comprises a platinum gas diffusion electrode, hot pressed or coated on one side with a polytetrafluoroethylene (PTFE) based cation exchange membrane or a sulfonated polytetrafluoroethylene based ion exchange membrane.

10 16. The method according to anyone of claims 10 and 15, wherein the cathode comprises or consists of nickel, palladium, rhodium, indium, cobalt, stainless steel or carbon.

15 17. A membrane-electrode assembly, comprising a metal gas diffusion electrode, hot pressed or coated with a, preferably hydrophobic, cation exchange material on one side.

20 18. The membrane-electrode assembly according to claim 17, wherein the membrane-electrode assembly comprises a platinum gas diffusion electrode, hot pressed or coated on one side with a polytetrafluoroethylene (PTFE) based cation exchange membrane or a sulfonated polytetrafluoroethylene based ion exchange membrane.

25

Fig. 1

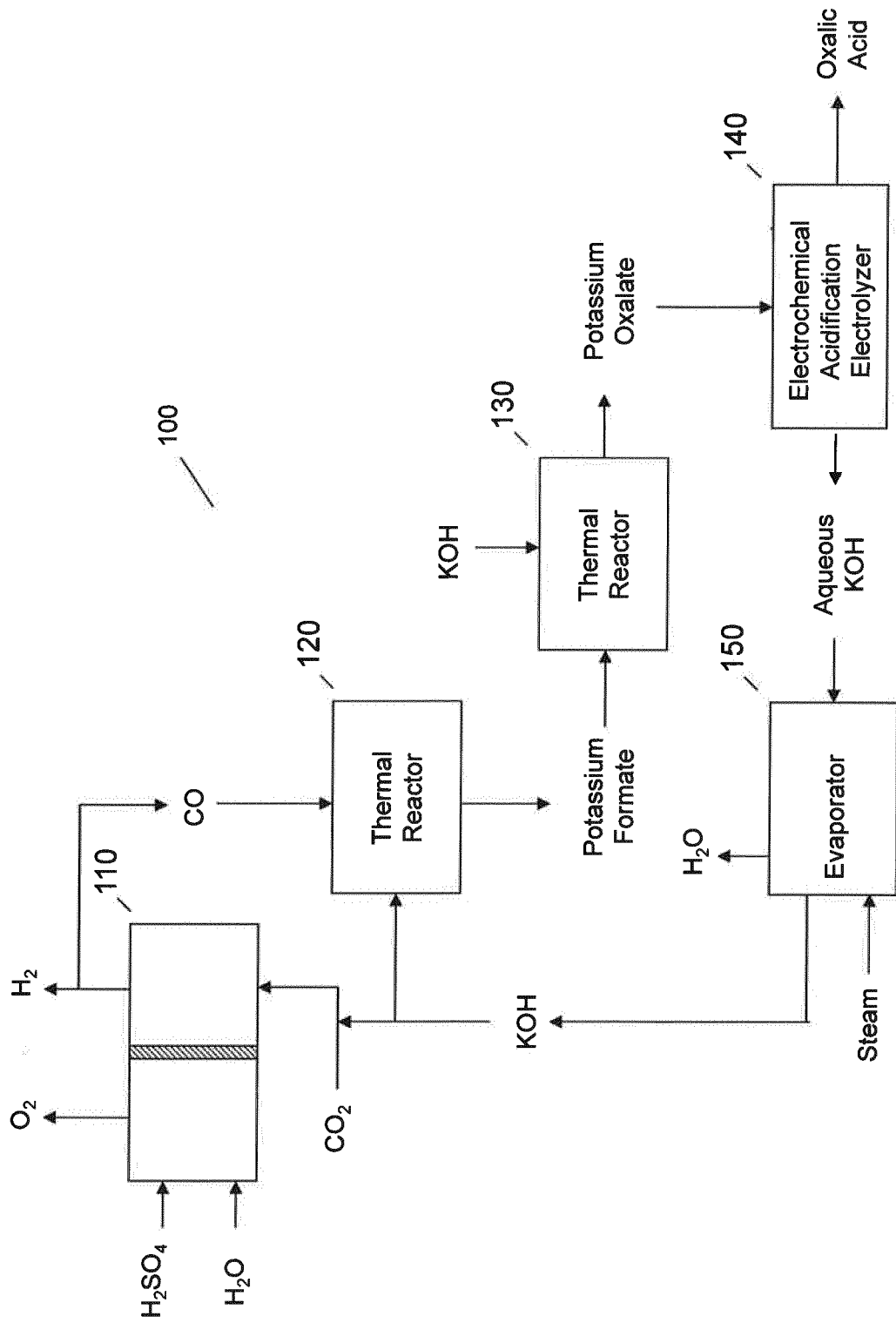


Fig. 2

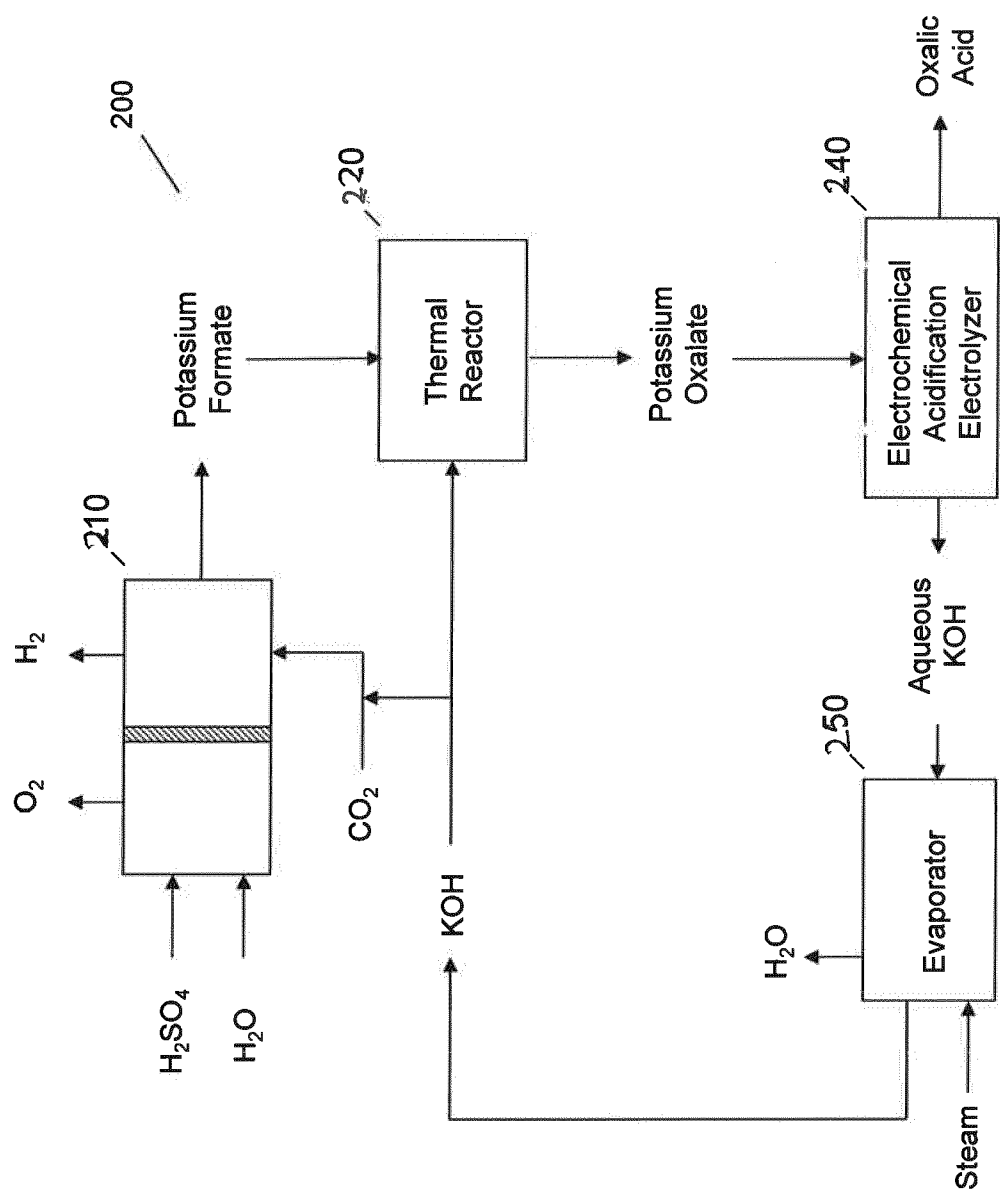
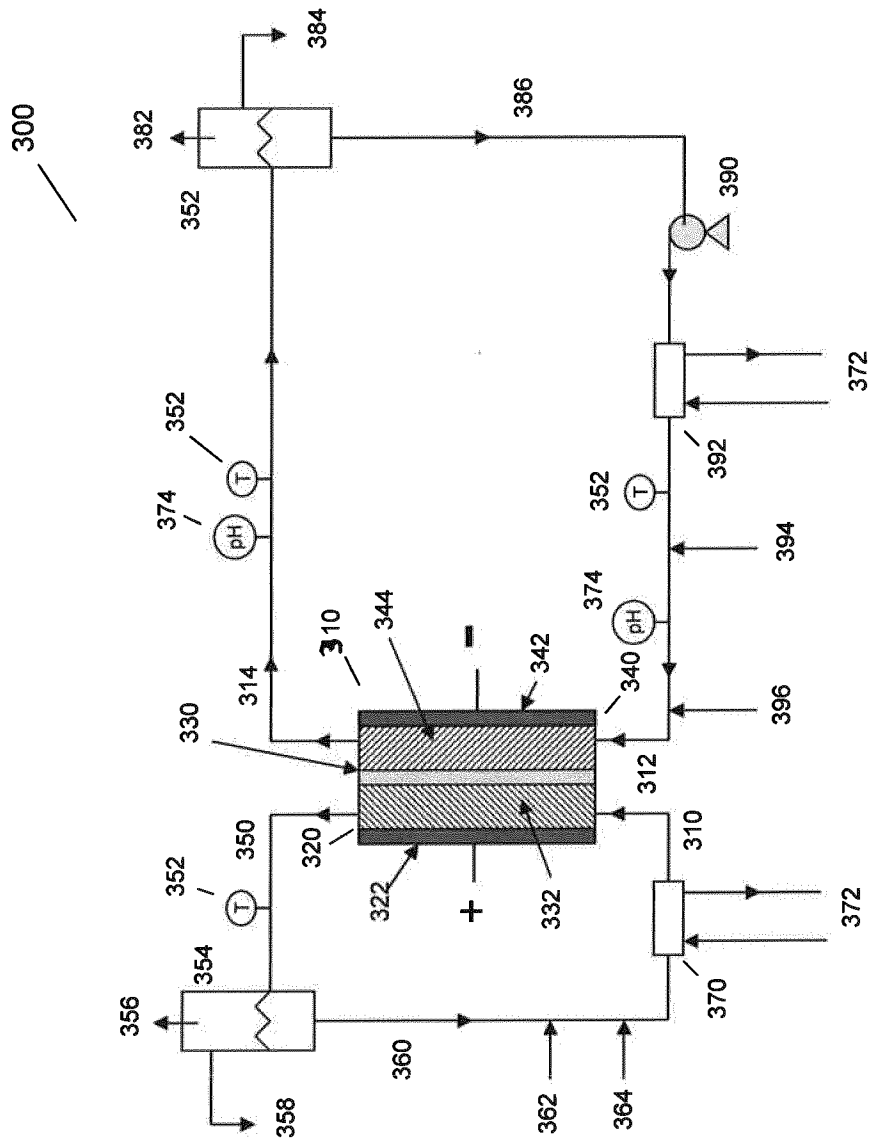




Fig. 3



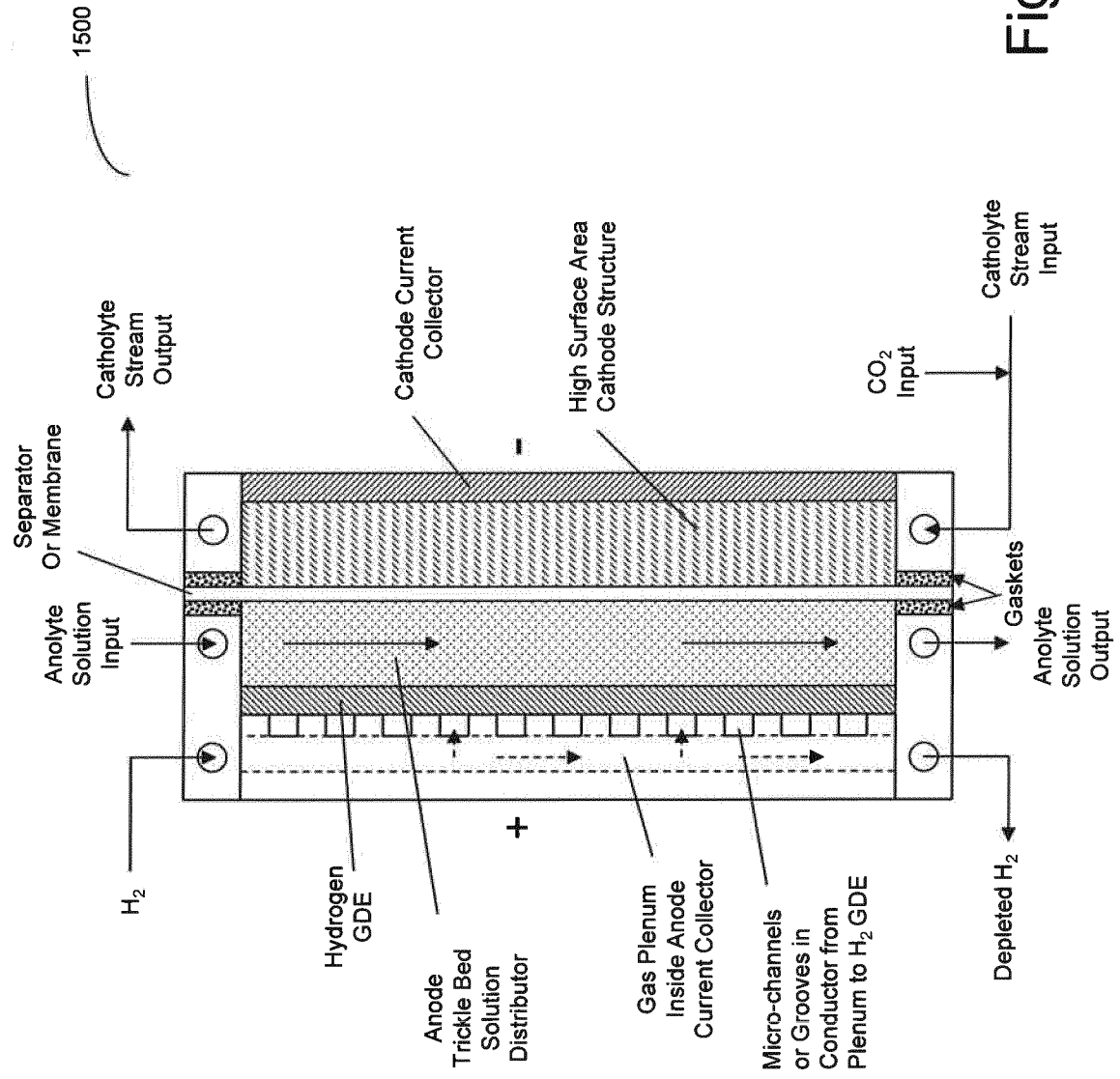


Fig. 4

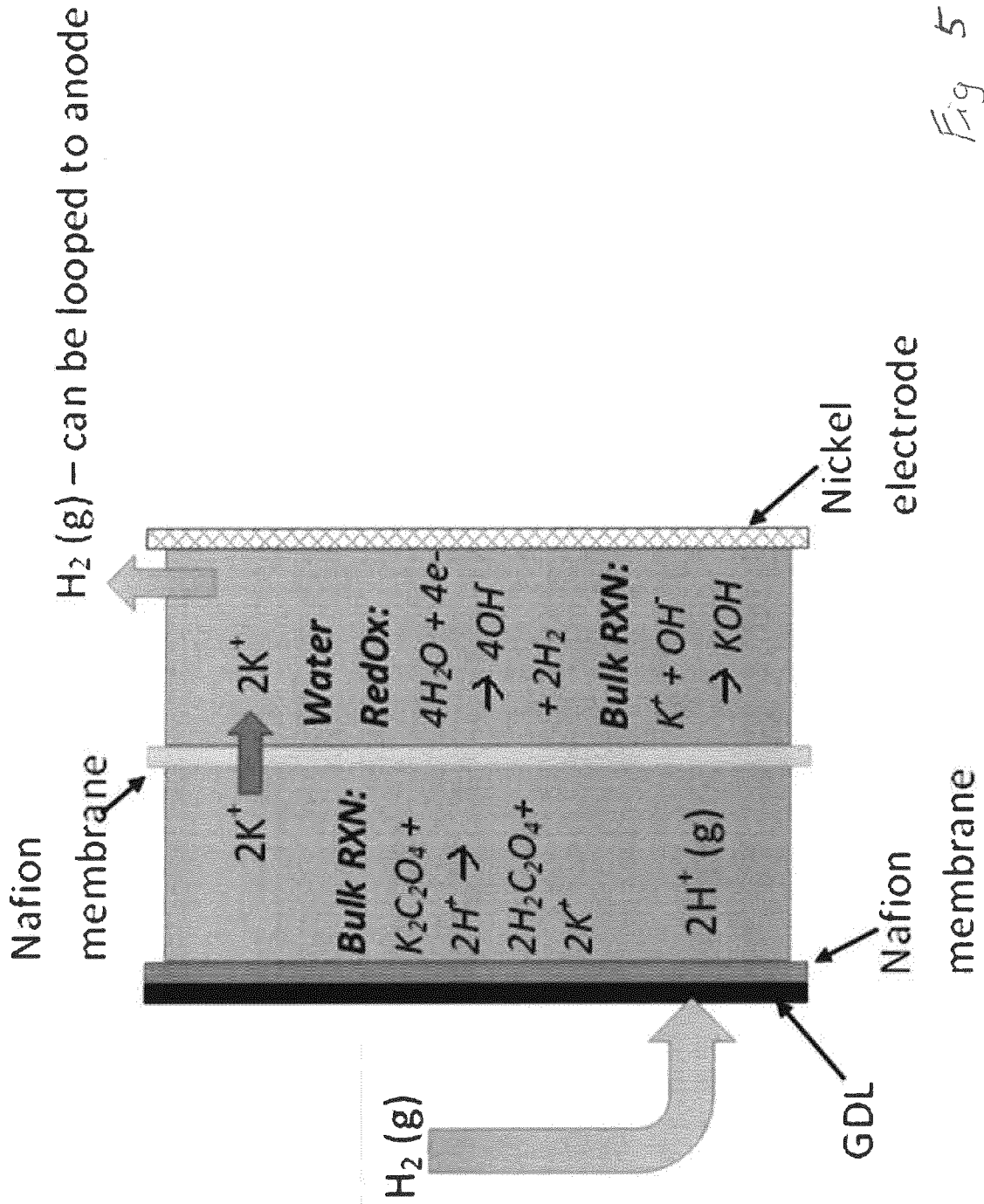


Fig 5

**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/EP2017/050234

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C25B11/03 C25B15/08 C25B3/04 C25B9/08  
 ADD.  
 According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**  
 Minimum documentation searched (classification system followed by classification symbols)  
 C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2015/184388 A1 (LIQUID LIGHT INC [US]) 3 December 2015 (2015-12-03) cited in the application paragraphs [0004], [0031] - [0036], [0039] - [0040], [0082], [0108] - [0125], [0234]; figures 2B,12-14 -----	1-18
X	US 5 980 724 A (ROBERTS DAVID G [US] ET AL) 9 November 1999 (1999-11-09) column 8, lines 25-39 column 12, lines 44-56 column 13, lines 47-64 -----	17,18
A	US 2013/105304 A1 (KACZUR JERRY J [US] ET AL) 2 May 2013 (2013-05-02) the whole document -----	1-18

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
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Date of the actual completion of the international search  11 April 2017	Date of mailing of the international search report  21/04/2017
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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No

PCT/EP2017/050234

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