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APPARATUS AND METHOD FOR PRODUCTION OF FORMATE FROM CARBON DIOXIDE

Abstract

An apparatus is adapted for the production of formate from carbon dioxide. The apparatus includes a reactor including a reduction cell and a production cell and a formate dehydrogenase catalyst immobilized in the production cell. A cathode solution circulates through the reduction cell and the production cell. The cathode solution includes a charge carrier. An anode solution circulates through the anode compartment. The charge carrier is reduced in the reduction cell and reoxidized in the production cell. The carbon dioxide is converted to formate in the production cell.

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Background/Summary

RELATED APPLICATIONS [0001] This document claims the benefit of U.S. Provisional Patent Application Ser. No. 63/553,116, filed on Feb. 13, 2024, and U.S. Provisional Patent Application Ser. No. 63/756,510, filed Feb. 10, 2025, the full disclosure of each are incorporated herein by reference.

TECHNICAL FIELD

[0002] This document relates to an apparatus and method for converting carbon dioxide to formate using an enzymatic catalyst.

BACKGROUND

[0003] While the shift to renewable energy continues, fossil fuel-based resources will nonetheless continue to be used for the foreseeable future. One way to mitigate emissions from such resources is by converting the emitted carbon dioxide (CO₂) into other usable products, such as formic acid. Formic acid has a number of useful applications, including in the fuel cell and liquid hydrogen storage fields. Furthermore, formic acid requires a minimum activation energy relative to other products and minimal water for CO₂ conversion. Formic acid, formaldehyde, and oxalic acid, are ranked highest among a myriad of other fuel products due to economic feasibility and high capacity to decrease CO₂ emissions.

[0004] The state-of-the-art process for formic acid production is the Kemira process, which first reforms methane into methanol, both of which are already valuable commodities, then reacts methanol with carbon monoxide, including heterogenous catalysis under elevated pressure and mild to high temperatures, followed by hydrolysis to form formic acid. Subsequently, distillation separates the formic acid from the methanol and any water. This overall process is energy intensive and can contribute to further carbon emissions. Alternatively, formic acid production can be done electrochemically, first converting CO₂ to formate, and then to formic acid in post-processing using techniques such as ion exchange. The electrochemical route for formate (referred to as such henceforth) production can circumvent the need for elevated temperatures/pressures while providing the capability for negative emissions.

[0005] A significant challenge arising from electrochemical processes is product selectivity from competing electrochemical reactions. Typically, this is done using metal catalysts, and the most popular catalysts for electrochemical reduction are lead, tin, and bismuth. The metal catalyst used will affect the products formed, such as carbon monoxide, hydrogen, and higher-order carbon products. However, the electrochemical conversion of CO₂ can be difficult to control and often generates unwanted side reactions. Some studies have reported efficiencies approaching 100% for different types of catalyst, but these are usually short-term. Long-term, stability remains a challenge, and protonation on the catalyst can expose a vulnerability to unwanted reactions such as hydrogen evolution, and thus form additional products.

[0006] This document relates to an apparatus and method for converting carbon dioxide to formate using an enzymatic catalyst, formate dehydrogenase 1 from *Methylobacterium extorquens* AM1 (MeFDH1), that provides a number of benefits and advantages over the state of the art devices and processes described above. The enzymatic catalyst, MeFDH1, produces high yields of the desired formate product, and operates reliably at near ambient temperature and pressure conditions at higher current densities that are used to accelerate formate production.

SUMMARY

[0007] In accordance with the purposes and benefits set forth herein, a new and improved apparatus

is provided for the production of formate from carbon dioxide. The apparatus comprises, consists of or consists essentially of: [0008] a reactor including a reduction cell and a production cell; [0009] a proton exchange membrane partitioning the reduction cell into an anode compartment and a cathode compartment; [0010] an anode in the anode compartment; [0011] a cathode in the cathode compartment; [0012] a voltage source connected across the anode and the cathode; [0013] a formate dehydrogenase catalyst immobilized in the production cell; [0014] a cathode solution circulating through the cathode compartment and the production cell, the cathode solution including a charge carrier; and [0015] an anode solution circulating through the anode compartment whereby (a) the charge carrier is reduced in the cathode compartment and reoxidized in the production cell and (b) carbon dioxide is converted to formate in the production cell.

[0016] In at least some of the many possible embodiments of the apparatus, the formate dehydrogenase catalyst is formate dehydrogenase 1 from *Methylobacterium extorquens* AM1 (MeFDH1). Preferably, the MeFDH1 is immobilized on agarose beads.

[0017] The charge carrier may be selected from a group consisting of ethyl viologen, methyl viologen dibromide, 1,1'-diheptyl-4,4'-bipyridinium dibromide, 1,1'-di-n-octyl-4,4'-bipyridinium dibromide, 1,1'-dibenzyl-4,4'-bipyridinium dichloride, 1,1'-bis(2,4-dinitrophenyl)-4,4'-bipyridinium dichloride, 1,1'-diphenyl-4,4'-bipyridinium dichloride, propyl viologen, butyl viologen, benzyl viologen, ethanol viologen, propanol viologen, methyl acetate viologen, acetate viologen, ethylamine viologen, propylamine viologen, and methyl ethylamine viologen, chloride salts thereof, bromide salts thereof and combinations thereof.

[0018] In at least some embodiments of the apparatus, the apparatus further comprises an oxygen scavenger in the cathode solution. The oxygen scavenger may be selected from a group consisting of sodium thiosulfate, ascorbic acid, ferrous carbonate, sodium sulphite, sodium bisulphite, sodium metabisulphite, tannin, sodium erythorbate, hydrazine/carbohydrazine, N, N-diethylhydroxylamine and combinations thereof.

[0019] In at least some embodiments of the apparatus, the apparatus further comprises a pH buffer in the cathode solution. The pH buffer may be selected from a group consisting of Tris buffer, Tris-Bis buffer, BES, buffer, MOPS buffer, TES buffer, HEPES buffer, MOPSO buffer, Imidazole (glyoxaline)-HCl buffer, potassium hydroxide, sodium hydroxide, potassium carbonate, potassium phosphate and mixtures thereof, adapted to maintain a pH of the cathode solution between pH 6 and pH 8.

[0020] The anode may be selected from a group consisting of a platinum wire mesh electrode, a platinum oxide coated carbon electrode, an iridium oxide coated carbon electrode, a cobalt oxide coated carbon electrode, a lead oxide/titanium alloy iridium-platinum coated carbon electrode, an iridium-ruthenium coated carbon electrode, and an iridium-tantalum coated carbon electrode. The cathode may be selected from a group consisting of a copper electrode, a tin-coated copper electrode, a bismuth-coated copper electrode, a lead-coated copper electrode, a bismuth-tin-lead alloys coated copper electrode, and bismuth-tin-lead alloys coated on porous carbon, carbon felt, carbon cloth, woven carbon, or carbon nanotube electrodes.

[0021] In accordance with yet another aspect, an apparatus adapted for production of formate from carbon dioxide, comprises, consists of or consists essentially of: [0022] a reactor including a reduction cell and a production cell; [0023] a formate dehydrogenase catalyst immobilized in the production cell; [0024] a cathode solution circulating through the reduction cell and the production cell, the cathode solution including a charge carrier; and [0025] an anode solution circulating through the anode compartment whereby (a) the charge carrier is reduced in the reduction cell and reoxidized in the production cell and (b) carbon dioxide is converted to formate in the production cell.

[0026] The formate dehydrogenase catalyst may be MeFDH1. The MeFDH1 may be immobilized on agarose beads. The apparatus may further comprise an oxygen scavenger and a pH buffer in the cathode solution.

[0027] In accordance with yet another aspect, a new and improved method of producing formate from carbon dioxide in a dual cell reactor, comprises, consists of or consists essentially of: [0028] circulating a charge carrier solution between a reduction cell and a production cell; [0029] reducing a charge carrier in the charge carrier solution in the reduction cell; [0030] reoxidizing the charge carrier in the production cell; and [0031] converting carbon dioxide and protons to formate in presence of a formate dehydrogenase catalyst in the production cell.

[0032] In at least some embodiments, the method further comprises one or more of the following steps: (a) partitioning the reduction cell into an anode compartment and a cathode compartment with a proton exchange membrane, (b) locating an anode in the anode compartment, (c) locating a cathode in the cathode compartment, and (d) applying a voltage across the anode and the cathode.

[0033] The method may further comprise circulating an oxygen scavenger with the charge carrier in the charge carrier solution. The method may further comprise circulating a pH buffer with the charge carrier in the charge carrier solution. The method may further comprise maintaining the charge carrier solution at a temperature between 20° C. and 40° C. and/or a pH of between pH 6 and pH 8. The method may further comprise maintaining the applied voltage between -0.75 V to -0.95 V vs. Ag/AgCl.

[0034] In accordance with still another aspect, a method of producing formate from carbon dioxide in a dual cell reactor, including a reduction cell and a production cell, comprises, consists of or consists essentially of: [0035] partitioning the reduction cell into an anode compartment and a cathode compartment with a proton exchange membrane; [0036] locating an anode in the anode compartment; [0037] locating a cathode in the cathode compartment; [0038] applying a voltage across the anode and the cathode; [0039] immobilizing a formate dehydrogenase catalyst in the production cell; [0040] circulating a cathode solution, including a charge carrier, through the cathode compartment and the production cell; and [0041] circulating an anode solution through the anode compartment whereby (a) the charge carrier is reduced in the cathode compartment and reoxidized in the production cell and (b) carbon dioxide is converted to formate in the production cell.

[0042] The method may further comprise circulating an oxygen scavenger with the charge carrier in the charge carrier solution. The method may further comprise circulating a pH buffer with the charge carrier in the charge carrier solution. The method may further comprise maintaining the charge carrier solution at a temperature between 20° C. and 40° C. and/or a pH of between pH 6 and pH 8. The method may further comprise maintaining the applied voltage between -0.75 V to -0.95 V vs. Ag/AgCl.

[0043] The above and other aspects and features are described and exemplified by the following figures and detailed description.

Description

BRIEF DESCRIPTION OF THE DRAWING FIGURES

[0044] The following descriptions should not be considered limiting in any way.

[0045] FIG. 1 is a schematic illustration of the apparatus adapted for production of formate from carbon dioxide using a reactor including a reduction cell and a production cell and a formate dehydrogenase catalyst.

[0046] FIG. 2 is a detailed schematic illustration of the reduction cell of the apparatus illustrated in FIG. 1.

[0047] FIG. 3 is a detailed schematic illustration of the production cell of the apparatus illustrated in FIG. 1.

[0048] FIG. 4 is an illustration of the catalyst activity that converts carbon dioxide and protons to formate.

[0049] FIG. 5A is a schematic illustration a vessel for the cathode solution in order to accommodate dosing with a pH buffer.

[0050] FIG. 5B is a schematic illustration of the cathode solution flow system.

DETAILED DESCRIPTION

[0051] Reference is now made to FIG. 1 which schematically illustrates one possible embodiment of the new and improved apparatus **10** adapted for converting carbon dioxide (CO₂) to formate (HCOO⁻). In the illustrated embodiment, the apparatus **10** includes a dual cell reactor **12**, comprising a reduction cell **14** and a production cell **16**.

[0052] As shown in FIG. 2, the reduction cell **14** includes two opposed end plates **18**, **20**. A cathode **22** is provided adjacent the end plate **18** and an anode **24** is provided adjacent the end plate **20**. A proton exchange membrane **26**, of a type known in the art, partitions the reduction cell **14** into an anode compartment **28**, between the membrane **26** and the end plate **20**, and a cathode compartment **30**, between the membrane **26** and the end plate **18**. Mesh sheets **32**, on each side of the membrane **26**, help support the membrane in position. Gaskets **34** seal the anode and cathode compartments **28**, **30** provided between the components.

[0053] As shown in FIG. 3, the production cell **16** includes two opposed end plates **36**, **38**. An immobilized formate dehydrogenase catalyst **40** is supported between the end plates **36**, **38** and sandwiched between mesh sheets **42**. Gaskets **44** seal the production cell **16**. Preferably, the formate dehydrogenase catalyst **40** is formate dehydrogenase 1 from *Methylobacterium extorquens* AM1 (MeFDH1) immobilized on agarose beads or other appropriate support material known to those skilled in the art. In at least some embodiments, the production cell **16** may comprise a packed bed reactor and for purposes of this document, the terminology “production cell” includes such a packed bed reactor.

[0054] The cathode **22** may be made from various materials. Porous, conductive, inert materials appear to be the most viable choices. Useful materials include, but not necessarily limited to, a copper electrode, a tin-coated copper electrode, a bismuth-coated copper electrode, a lead-coated copper electrode, a bismuth-tin-lead alloys coated copper electrode, and bismuth-tin-lead alloys coated on porous carbon, carbon felt, carbon cloth, woven carbon, or carbon nanotube electrodes. The anode **24** may comprise a platinum wire mesh electrode, a platinum oxide coated carbon electrode, an iridium oxide coated carbon electrode, a cobalt oxide coated carbon electrode, a lead oxide/titanium alloy iridium-platinum coated carbon electrode, an iridium-ruthenium coated carbon electrode, and an iridium-tantalum coated carbon electrode.

[0055] A voltage source, generally designated by reference number **46**, is connected across the cathode **22** and the anode **24**. In the illustrated embodiment, the voltage source **46** includes a potentiostat **48** and a data logger **50**.

[0056] An anode solution **52** is circulated by a pump **54** from the anode solution reservoir **56** through the anode compartment **28**, across the anode, and then back to the anode solution reservoir. The anode solution **52** may comprise a sulfuric acid solution to serve as a proton source for converting carbon dioxide into formate. Other anode solutions, serving as proton donors, include, but are not necessarily limited to, hydrochloric acid, acetic acid, formic acid, carbonic acid, citric acid, ascorbic acid, and nitric acid.

[0057] A cathode solution or charge carrier solution **60** is circulated by the pump **62** from the cathode solution reservoir **64** through the cathode compartment **30**, across the cathode **22**, and then to the production cell **16** and, finally, back to the cathode solution reservoir. In the most preferred embodiment, the cathode solution includes a charge carrier, an oxygen scavenger and a pH buffer.

[0058] In one possible embodiment, the charge carrier is ethyl viologen (EV), the oxygen scavenger is sodium thiosulfate, and the pH buffer is potassium carbonate. The charge carrier is adapted to facilitate the conversion of carbon dioxide by first being electrochemically reduced in the cathode compartment **30** of the reduction cell **14** at a sufficient voltage (~-0.7 V vs. Ag/AgCl) to an EV^{•+} species, then donating its charge to the catalyst enzyme **40** in the production cell **16**

to produce formate, while reoxidizing back to dissolved EV_{sup.2+} in the process. The oxygen scavenger functions to eliminate competition with dissolved oxygen (O_{sub.2}) present in the cathode solution: that is, decreases the use of applied current for undesired chemical reactions. The pH buffer maintains the pH of the cathode solution within a desired range of pH 6 to pH 8; that is, the pH range most conducive to the catalytic activity and service life of the MeFDH1 catalyst **40**. The concentration of the charge carrier in the cathode solution may range from about 1-100 mM, or 1-50 mM, or 1-25 mM, or 1-20 mM or 10 mM.

[0059] Charge carriers useful in the apparatus **10** include, but are not necessarily limited to, ethyl viologen, methyl viologen dibromide, 1,1'-diheptyl-4,4'-bipyridinium dibromide, 1,1'-di-n-octyl-4,4'-bipyridinium dibromide, 1,1'-dibenzyl-4,4'-bipyridinium dichloride, 1,1'-bis(2,4-dinitrophenyl)-4,4'-bipyridinium dichloride, 1,1'-diphenyl-4,4'-bipyridinium dichloride, propyl viologen, butyl viologen, benzyl viologen, ethanol viologen, propanol viologen, methyl acetate viologen, acetate viologen, ethylamine viologen, propylamine viologen, and methyl ethylamine viologen, chloride salts thereof, bromide salts thereof and combinations thereof.

[0060] Oxygen scavengers useful in the apparatus **10** include, but are not necessarily limited to, sodium thiosulfate, ascorbic acid, ferrous carbonate, sodium sulphite, sodium bisulphite, sodium metabisulphite, tannin, sodium erythorbate, hydrazine/carbohydrazine, N, N-diethylhydroxylamine and combinations thereof.

[0061] The pH buffers useful in the apparatus **10** include, but are not necessarily limited to, Tris buffer, Tris-Bis buffer, BES, buffer, MOPS buffer, TES buffer, HEPES buffer, MOPSO buffer, Imidazole (glyoxaline)-HCl buffer, potassium hydroxide, sodium hydroxide, potassium carbonate, potassium phosphate and mixtures thereof, adapted to maintain a pH of the cathode solution between pH 6 and pH 8. The concentration of the oxygen scavenger in the cathode solution may range from about 1-100 mM, or 5-95 mM, or 10-50 mM, or 20-40 mM. In some embodiments, the cathode solution reservoir **64** may include structure to accommodate dosing the cathode solution **60** with potassium hydroxide (KOH). See FIG. 5A. FIG. 5B illustrates the flow system components in the order through which the cathode solution flows. In such an embodiment, the cathode solution may first be pumped into the production cell **16**, then into the reduction cell **14** so that the cathode solution reservoir **64** is capable of measuring pH immediately before entering the production cell. Such a configuration is particularly useful when the production cell **16** is a packed bed reactor.

[0062] The apparatus **10** described herein is useful in a method of producing formate from carbon dioxide in a dual cell reactor **12** including a reduction cell **14** and a production cell **16**. The method may include steps of: (a) partitioning the reduction cell **14** into an anode compartment **28** and a cathode compartment **30** with a proton exchange membrane **26**, (b) locating an anode **24** in the anode compartment, (c) locating a cathode **22** in the cathode compartment, (d) applying a voltage across the anode and the cathode, (e) immobilizing a formate dehydrogenase catalyst **40** in the production cell, (f) circulating a cathode solution **60**, including a charge carrier, through the cathode compartment and the production cell, and (g) circulating an anode solution **52** through the anode compartment whereby (i) the charge carrier is reduced in the cathode compartment and reoxidized in the production cell and (ii) carbon dioxide is converted to formate in the production cell.

[0063] The method may further comprise one or more of the following steps: (a) circulating an oxygen scavenger with the charge carrier in the charge carrier solution, (b) circulating a pH buffer with the charge carrier in the charge carrier solution, (c) maintaining the charge carrier solution at a temperature between 20° C. and 40° C., or 25° C. and 35° C. or at 30° C., (d) maintaining the cathode solution at a pH of between pH 6 and pH 8 or pH 6.5 and pH 7.5, or pH 6.3 and pH 6.8, and (e) maintaining the applied voltage between -0.75 V to -0.95 V vs. Ag/AgCl or -0.8 to -0.9 V vs. Ag/AgCl, or at -0.85 V vs. Ag/AgCl.

[0064] The apparatus **10** and method advantageously decouple the electrochemical charge carrier reduction and subsequent catalyst interaction into two separate processes, each in their own unit

cell. If done in a flow cell configuration, the system would have two primary benefits. One would be that the product catalyst in the production cell **16** would be protected from high overpotentials in the electrode. The configuration would also greatly reduce the chance of fouling deposits from the enzyme accumulating in the reduction cell **14** and subsequently weakening its performance.

Experimental Section

[0065] The flow system initially considered in the study involved two cells **14**, **16** consisting of stainless steel end plates **18**, **20** and **36**, **38** hand-tightened with sufficiently shaped, compressed gaskets **34**, **44** (See FIG. 1). The contact area which the solution could interact with either the electrodes (reduction cell) **22**, **24** or enzyme (production cell) **40** was approximately 33 cm.² in both cells. In the reduction cell **14**, a Nafion [®] 115 membrane **26** separated the two streams in the anode and cathode compartments **28**, **30**. The anode side or compartment **28** used a platinum-iridium coated electrode **24** (average loading 0.7 mg/cm.² on carbon) and circulated a 100 mM aqueous H₂SO₄ solution **52**. The dissociated protons from the sulfuric acid replenished by the oxygen evolution reaction serve as a proton source through the Nafion membrane **26**, and travel to the production cell **16** to react with CO₂ and EV⁺ in the enzyme catalyst **40** to produce formate. In the absence of an applied current between both cells, charge neutrality is conserved by the presence of other species, including HCO₃⁻, CO₃²⁻, OH⁻, Cl⁻, HCOO⁻, K⁺, H⁺, EV₂⁺, EV⁺, EV₂₂⁺, and EVH⁺. Therefore, the protons can remain in the solution into the production cell **16**, although this will alter the concentration of some other ionic species.

[0066] The cathode side or compartment **30** used a carbon felt electrode **22**, of a type commonly used in batteries, and a 200 mM potassium carbonate (KHCO₃) buffer. Using the carbon felt electrode **22** increased current density on average by over 10× for the same applied voltage, which may result in larger formate production rates over traditional copper electrodes that typically produce a wide array of other products. Both cathode and anode solutions **60**, **52** were initially filled with a 100 mL volume. The cathode volume doubled to 200 mL when a pH buffer was employed to balance the proton flux from the anode **24**, which diluted the charge mediator/carrier concentration. The charge mediator used in this study is 10 mM ethyl viologen (EV). The pH buffer was only employed during the third set of testing when the packed bed reactor was present.

[0067] In the reduction cell **14** (FIG. 2), the anode solution **52** was circulated on the bottom side and the cathode **22** at the top, to minimize cathode transit time between the two cells. Unless otherwise stated, the default flow rate used during most experiments was 10 mL/min. The production cell **16** (FIG. 3) was essentially a bioelectrochemical cell, with no external wiring connections and served to house the catalyst **40**. The catalyst **40** would receive reduced EV⁺ from the reduction cell **14**, along with CO₂ and H⁺, to produce HCOO⁻, converting the reduced EV⁺ back to EV₂⁺ in the process (See FIG. 4). The production cell **16** was placed at a higher elevation than the reduction cell **14** and operated in a flow-through mode. From the production cell **16**, one pathway would be to separate the formate from the solution and perform an additional protonation step using available technologies such as ion exchange (IEX) to produce a purified formic acid stream.

[0068] The pump pressure was used to oppose gravitational effects, which in this configuration, would ensure that the catholyte **60** would maximize its contact with the enzyme **40** in the production cell **16**. Initially, microfiltration membranes were used, but they resulted in high pressure increases in the system even at small flow rates. Darcy's law was used to relate flow rate and pressure:

$$[00001] \quad P = \frac{\mu L Q}{k} \quad (1)$$

where μ represents the fluid viscosity, L is the length through which a pressure increase is expected, and Q is the flow rate. The permeability constant, k , was determined. All values obtained were on the order of 10⁻¹⁹ m.², in line with impervious surfaces such as granite. Such results

verified the difficulty of using high filtration membranes, even for water with viscosity of approximately 1 mPa·s. The size of the immobilized agarose beads attached to the catalyst **40** enabled it to be used in a much larger mesh, which kept the overall system pressure at more manageable levels. Ultimately, it was determined that the catalyst **40** was large enough to be contained in a 121×121 size mesh membrane (McMaster-Carr).

[0069] The CO₂ reduction catalyst **40** in the production cell **16** was a formate dehydrogenase 1 from *Methylobacterium extorquens* AM1 (MeFDH1). An affinity tag was used to immobilize the enzyme by binding it onto agarose beads. Kinetic studies determined the enzyme's most favorable operating conditions, suggesting that temperatures above ambient would decrease activity. An econo-column (Bio-Rad) enabled that the enzyme detached from the beads, where UV-vis could be used to confirm the enzyme's optimal pH range of 6.3<pH<6.8. The enzyme samples were preserved in a MOPS (3-(N-morpholino) propanesulfonic acid) buffer and stored at 4° C. The approximate enzyme activity used in the experiment was 6.7 μM, or approximately 200 U.

[0070] The cathode solution **60** initially consisted of 200 mM potassium bicarbonate (KHCO₃) buffer with 10 mM ethyl viologen (EV). To minimize the contribution of dissolved atmospheric molecular oxygen present in the cathode solution, a 5 mM oxygen scavenger (sodium thiosulfate) was also employed. The scavenger served to decrease the contribution of the current for unwanted reactions and therefore improves the CO₂ to formate conversion efficiency. The EV charge carrier was reduced in the reduction cell **14** and then reoxidized in the production cell **16** upon interaction with the catalyst **40** to produce formate. This formate was released by the catalyst back into the bulk solution where liquid samples could be drawn to determine the quantity produced. Samples were analyzed with ion chromatography (IC), mixed with a 6 M sulfuric acid solution to prevent the produced formate from reoxidizing. Samples in the flow system were collected at intervals sufficient to evaluate the formate production changes over time.

[0071] Voltage was applied using a Gamry REF-600 potentiostat **48**. The system pressure was measured using an Omega PX-409 transducer. System voltages, along with pH, were also recorded using an external MIDI GL220 data logger **50**. A pH buffer has also been implemented to offset pH drops in the system which could denature the enzymes **40**, either due to increased presence of protons in the cathode side or production of formate, due to its low pKa number.

[0072] The pH controller **70** and pump **72** used to maintain the pH in the cathode compartment **30** by gradual dosing of potassium hydroxide (KOH)

[0073] The second set of experiments sought to enable better contact with EV in the production cell **16** to produce formate. Here, the production cell in FIG. 1 was replaced with a packed bed column. This column served a similar function as the production cell **16**, with the catalyst **40** secured through the same 121×121 mesh membrane. The catalyst was embedded in between volumes of sand to better distribute contact with the packed bed. To determine the dependence of pressure with sand packing on hydrodynamic conditions, the Ergun equation was used:

$$[00002] \quad P = \frac{150}{D_p^2} \frac{L(1-\epsilon)^2}{\epsilon^3} v_s + \frac{1.75L}{D_p} \frac{(1-\epsilon)}{\epsilon^3} v_s^2 \quad (2)$$

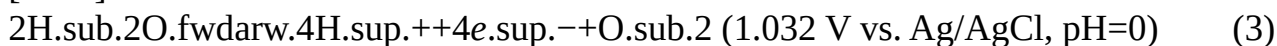
where μ again represents fluid viscosity, L is the length of the bed, $D_{sub.p}$ is the packing spherical diameter, ϵ is the bed porosity, $v_{sub.s}$ is the velocity of the fluid entering the bed, and ρ is the fluid density. $D_{sub.p}$ was obtained as 0.3 mm using known properties of the packing sand used, while porosity was obtained using the void/pore volume fractions. When the enzyme/catalyst **40** was included in the system, this porosity value was estimated at 0.1, but other values are included for reference. It should be noted that the variation in pressure with flow rate appears entirely linear; we attribute this to the extremely small velocities obtained in the system through the packed bed (reaching no more than 1 mm/s, corresponding to entirely laminar flow). The Ergun equation predicted pressure increases to over 200 kPa. This result is coupled with the initial equation based on the membrane selected, and suggests that, coupled with a microfiltration membrane, porosity should be kept high enough to prevent over-pressurizing the system. Thus, if system pressure is

minimal, pumping energy for the system will be low, and thus not as major a concern when considering energy costs for dual-cell configuration long-term. This confirms that pressure and corresponding energy requirements for the system are decreased compared with microfiltration. [0074] During optimal operation, the following reactions are expected to take place within the system:

Anode:

Oxygen Evolution/Proton Formation:

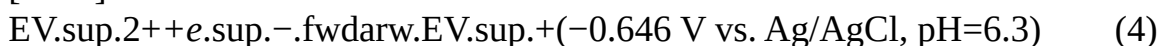
[0075]



Cathode, Reduction Cell:

First Reduction of EV:

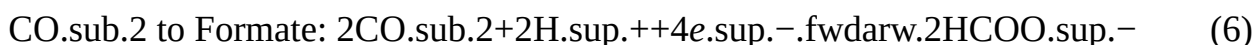
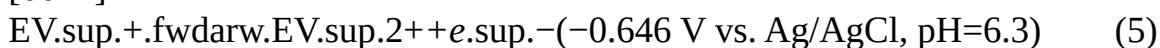
[0076]



Cathode, Production Cell:

Re-Oxidation of EV:

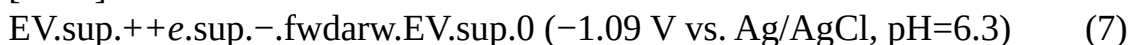
[0077]



[0078] While the initial buffer (KHCO_3) is alkaline and purging the system with CO_2 decreases the pH, the pH remains >6 and the product is formate. Additional, unwanted side reactions may also take place on the cathode side of the reduction cell:

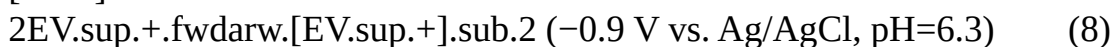
Second Reduction of EV:

[0079]



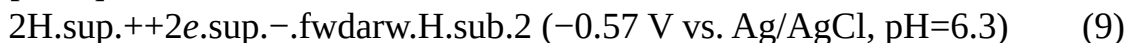
Dimerization of EV:

[0080]



Hydrogen Evolution:

[0081]



[0082] Dimerization of EV, however, has been shown to be minimal, particularly when compared with other charge carriers such as methyl viologen. Hydrogen, while also a desired product in electrochemical fuel production, is neither analyzed nor captured in this study.

[0083] The Coulombic efficiency (CE) of the system is calculated by relating the molar formate production in the system to the total electronic input. As a percentage, this value is expressed as:

$$[00003] \text{ CE} = \frac{(\text{molHCOO}^-)(\text{\#electronsrequired})(\text{Faradayconstant})}{(\text{ChargeInput})} * 100\% \quad (10)$$

where the number of moles of formate produced is found by taking its concentration and multiplying by the solution volume in the system. The electrochemical conversion of CO_2 into formate requires 2 electrons (Eq. 6). Charge input is given in Coulombs:

$$[00004] \text{ ChargeInput} = \int I(t)dt \quad (11)$$

where I represents the input current (in A). For Eq. 10, an absolute value of this quantity is taken since the applied current is negative, typically consistent with system potential.

[0084] In summary, we report on the unique design and construction of a dual-cell flow system which electrochemically converts CO_2 to formate first using an electrochemical reduction of a charge carrier, then having said reduced charge carrier reoxidize with an enzymatic catalyst to produce HCOO^- . The two processes are carried out in separate cells within the reactor. This is believed to be a first of its kind configuration that demonstrates successful conversion to formate and can be implemented into a range of different systems.

[0085] Each of the following terms written in singular grammatical form: “a”, “an”, and “the”, as used herein, means “at least one”, or “one or more”. Use of the phrase “One or more” herein does not alter this intended meaning of “a”, “an”, or “the”. Accordingly, the terms “a”, “an”, and “the”, as used herein, may also refer to, and encompass, a plurality of the stated entity or object, unless otherwise specifically defined or stated herein, or, unless the context clearly dictates otherwise. For example, the phrase: “a charge carrier”, as used herein, may also refer to, and encompass, a plurality of charge carriers.

[0086] Each of the following terms: “includes”, “including”, “has”, “having”, “comprises”, and “comprising”, and, their linguistic/grammatical variants, derivatives, or/and conjugates, as used herein, means “including, but not limited to”, and is to be taken as specifying the stated component(s), feature(s), characteristic(s), parameter(s), integer(s), or step(s), and does not preclude addition of one or more additional component(s), feature(s), characteristic(s), parameter(s), integer(s), step(s), or groups thereof.

[0087] The phrase “consisting of”, as used herein, is closed-ended and excludes any element, step, or ingredient not specifically mentioned. The phrase “consisting essentially of”, as used herein, is a semi-closed term indicating that an item is limited to the components specified and those that do not materially affect the basic and novel characteristic(s) of what is specified.

[0088] Terms of approximation, such as the terms about, substantially, approximately, etc., as used herein, refers to $\pm 10\%$ of the stated numerical value.

[0089] Although the apparatus and method of this disclosure have been illustratively described and presented by way of specific exemplary embodiments, and examples thereof, it is evident that many alternatives, modifications, or/and variations, thereof, will be apparent to those skilled in the art. Accordingly, it is intended that all such alternatives, modifications, or/and variations, fall within the spirit of, and are encompassed by, the broad scope of the appended claims.

Claims

1. An apparatus adapted for production of formate from carbon dioxide, comprising: a reactor including a reduction cell and a production cell; a proton exchange membrane partitioning the reduction cell into an anode compartment and a cathode compartment; an anode in the anode compartment; a cathode in the cathode compartment; a voltage source connected across the anode and the cathode; a formate dehydrogenase catalyst immobilized in the production cell; a cathode solution circulating through the cathode compartment and the production cell, the cathode solution including a charge carrier; and an anode solution circulating through the anode compartment whereby (a) the charge carrier is reduced in the cathode compartment and reoxidized in the production cell and (b) carbon dioxide is converted to formate in the production cell.
2. The apparatus of claim 1, wherein the formate dehydrogenase catalyst is formate dehydrogenase 1 from *Methylobacterium extorquens* AM1.
3. The apparatus of claim 2, wherein the formate dehydrogenase 1 from *Methylobacterium extorquens* AM1 is immobilized on agarose beads.
4. The apparatus of claim 1, wherein the charge carrier is selected from a group consisting of ethyl viologen, methyl viologen dibromide, 1,1'-diheptyl-4,4'-bipyridinium dibromide, 1,1'-di-n-octyl-4,4'-bipyridinium dibromide, 1,1'-dibenzyl-4,4'-bipyridinium dichloride, 1,1'-bis(2,4-dinitrophenyl)-4,4'-bipyridinium dichloride, 1,1'-diphenyl-4,4'-bipyridinium dichloride, propyl viologen, butyl viologen, benzyl viologen, ethanol viologen, propanol viologen, methyl acetate viologen, acetate viologen, ethylamine viologen, propylamine viologen, and methyl ethylamine viologen, chloride salts thereof, bromide salts thereof and combinations thereof.
5. The apparatus of claim 1, further including an oxygen scavenger in the cathode solution.
6. The apparatus of claim 5, wherein the oxygen scavenger is selected from a group consisting of sodium thiosulfate, ascorbic acid, ferrous carbonate, sodium sulphite, sodium bisulphite, sodium

metabisulphite, tannin, sodium erythorbate, hydrazine/carbohydrazine, N,N-diethylhydroxylamine and combinations thereof.

7. The apparatus of claim 1, further including a pH buffer in the cathode solution.

8. The apparatus of claim 7, wherein the pH buffer is selected from a group consisting of Tris buffer, Tris-Bis buffer, BES, buffer, MOPS buffer, TES buffer, HEPES buffer, MOPSO buffer, Imidazole (glyoxaline)-HCl buffer, potassium hydroxide, sodium hydroxide, potassium carbonate, potassium phosphate and mixtures thereof, adapted to maintain a pH of the cathode solution between pH 6 and pH 8.

9. The apparatus of claim 1, wherein the anode is selected from a group consisting of a platinum wire mesh electrode, a platinum oxide coated carbon electrode, an iridium oxide coated carbon electrode, a cobalt oxide coated carbon electrode, a lead oxide/titanium alloy iridium-platinum coated carbon electrode, an iridium-ruthenium coated carbon electrode, and an iridium-tantalum coated carbon electrode.

10. The apparatus of claim 1, wherein the cathode is selected from a group consisting of a copper electrode, a tin-coated copper electrode, a bismuth-coated copper electrode, a lead-coated copper electrode, a bismuth-tin-lead alloys coated copper electrode, and bismuth-tin-lead alloys coated on porous carbon, carbon felt, carbon cloth, woven carbon, or carbon nanotube electrodes.

11. An apparatus adapted for production of formate from carbon dioxide, comprising: a reactor including a reduction cell and a production cell; a formate dehydrogenase catalyst immobilized in the production cell; a cathode solution circulating through the reduction cell and the production cell, the cathode solution including a charge carrier; and an anode solution circulating through the anode compartment whereby (a) the charge carrier is reduced in the reduction cell and reoxidized in the production cell and (b) carbon dioxide is converted to formate in the production cell.

12. The apparatus of claim 11, wherein the formate dehydrogenase catalyst is formate dehydrogenase 1 from *Methylobacterium extorquens* AM1.

13. The apparatus of claim 12, wherein the formate dehydrogenase 1 from *Methylobacterium extorquens* AM1 is immobilized on agarose beads.

14. The apparatus of claim 13, further including an oxygen scavenger and a pH buffer in the cathode solution.

15. A method of producing formate from carbon dioxide in a dual cell reactor, comprising: circulating a charge carrier solution between a reduction cell and a production cell; reducing a charge carrier in the charge carrier solution in the reduction cell; reoxidizing the charge carrier in the production cell; and converting carbon dioxide and protons to formate in presence of a formate dehydrogenase catalyst in the production cell.

16. The method of claim 15, further comprising: partitioning the reduction cell into an anode compartment and a cathode compartment with a proton exchange membrane; locating an anode in the anode compartment; locating a cathode in the cathode compartment; and applying a voltage across the anode and the cathode.

17. The method of claim 15, further comprising circulating an oxygen scavenger with the charge carrier in the charge carrier solution.

18. The method of claim 17, further comprising circulating a pH buffer with the charge carrier in the charge carrier solution.

19. The method of claim 18, further comprising maintaining the charge carrier solution at a temperature between 20° C. and 40° C. and a pH of between pH 6 and pH 8.

20. The method of claim 19, including maintaining the applied voltage between -0.75 V to -0.95 V vs. Ag/AgCl.

21. A method of producing formate from carbon dioxide in a dual cell reactor including a reduction cell and a production cell, the method comprising: partitioning the reduction cell into an anode compartment and a cathode compartment with a proton exchange membrane; locating an anode in the anode compartment; locating a cathode in the cathode compartment; applying a voltage across

the anode and the cathode; immobilizing a formate dehydrogenase catalyst in the production cell; circulating a cathode solution, including a charge carrier, through the cathode compartment and the production cell; and circulating an anode solution through the anode compartment whereby (a) the charge carrier is reduced in the cathode compartment and reoxidized in the production cell and (b) carbon dioxide is converted to formate in the production cell.
