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(54) **PROCESS FOR THE PRODUCTION OF CHEMICALS**

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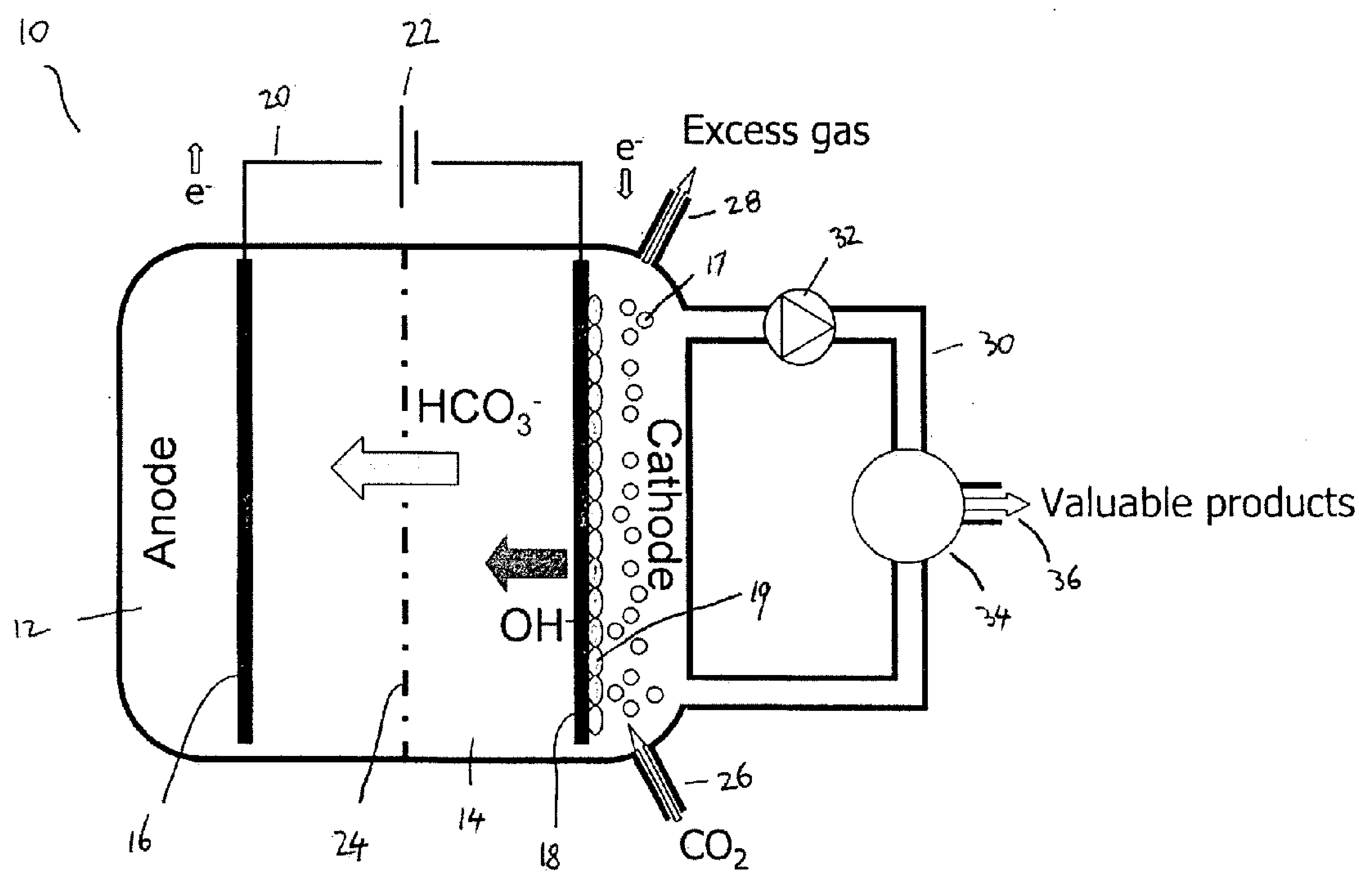
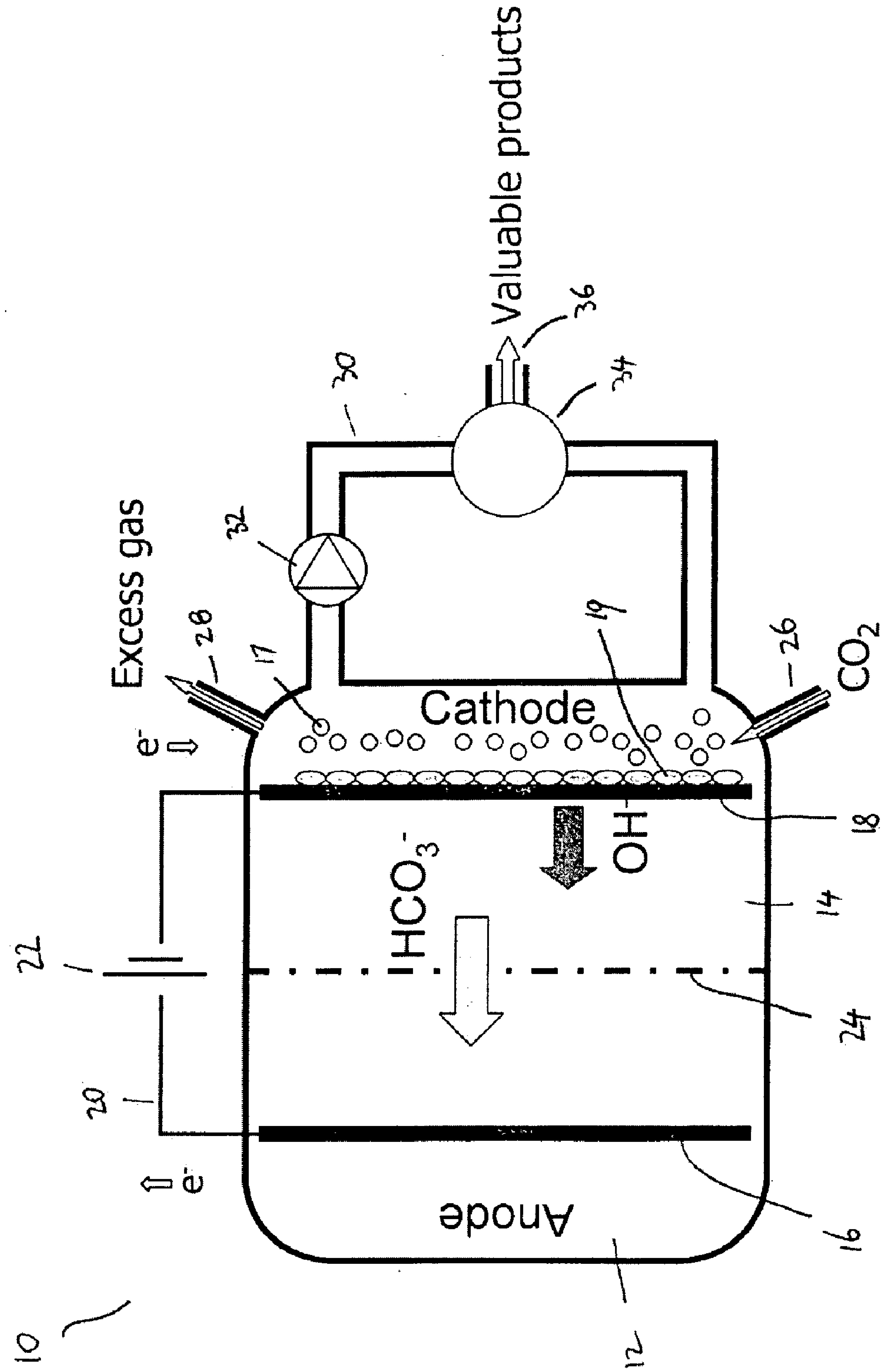
(57) **ABSTRACT**

A process for producing one or more chemical compounds comprising the steps of providing a bioelectrochemical system having an anode and a cathode separated by a membrane, the anode and the cathode being electrically connected to each other, causing oxidation to occur at the anode and causing reduction to occur at the cathode to thereby produce reducing equivalents at the cathode, providing the reducing equivalents to a culture of microorganisms, and providing carbon dioxide to the culture of microorganisms, whereby the microorganisms produce the one or more chemical compounds, and recovering the one or chemical compounds.




Valuable products
Excess gas
Cathode
Anode
CO_2
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HCO_3^-
e^-
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FIGURE 1

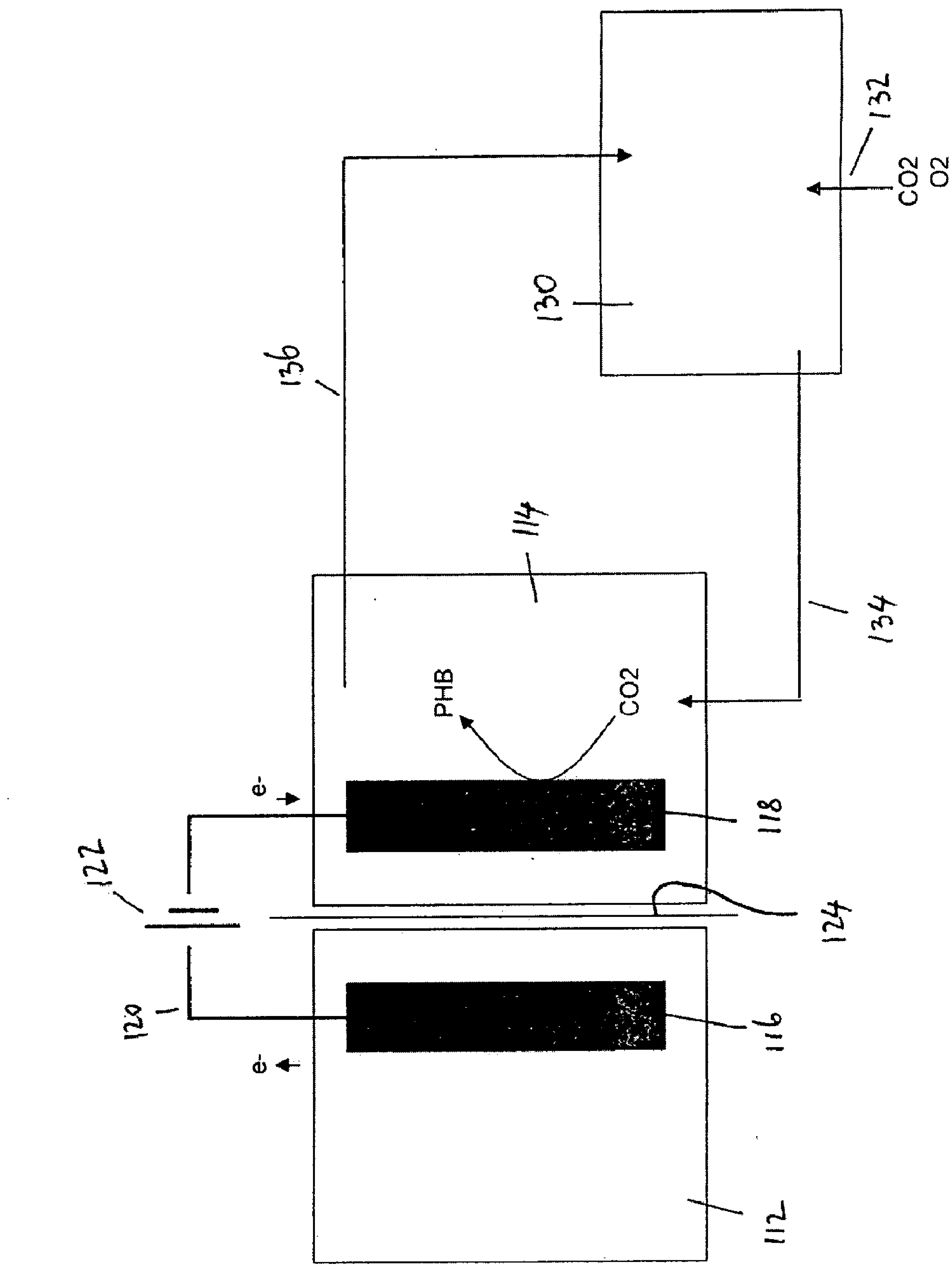
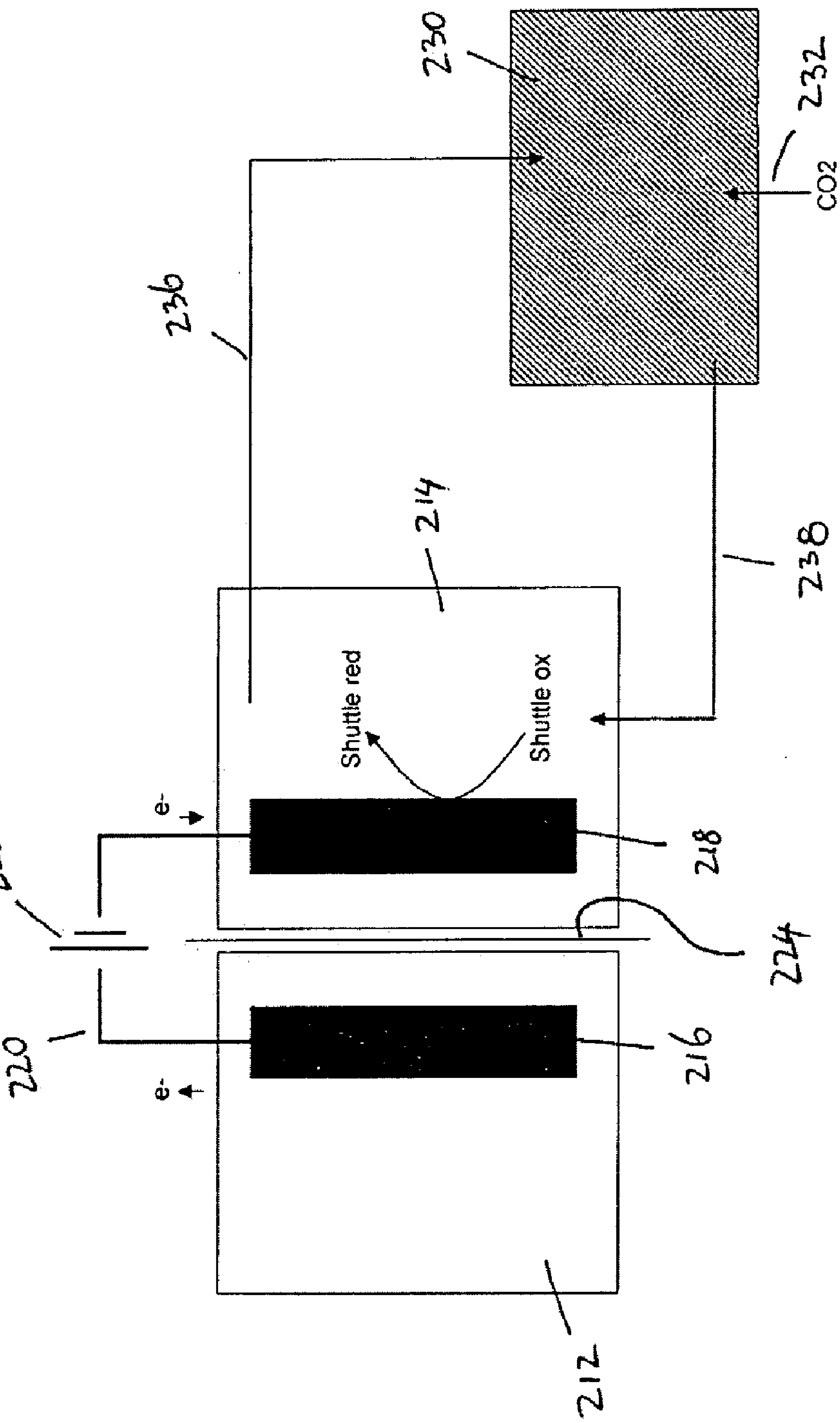


FIGURE 2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214
238
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e-
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212

FIGURE 3

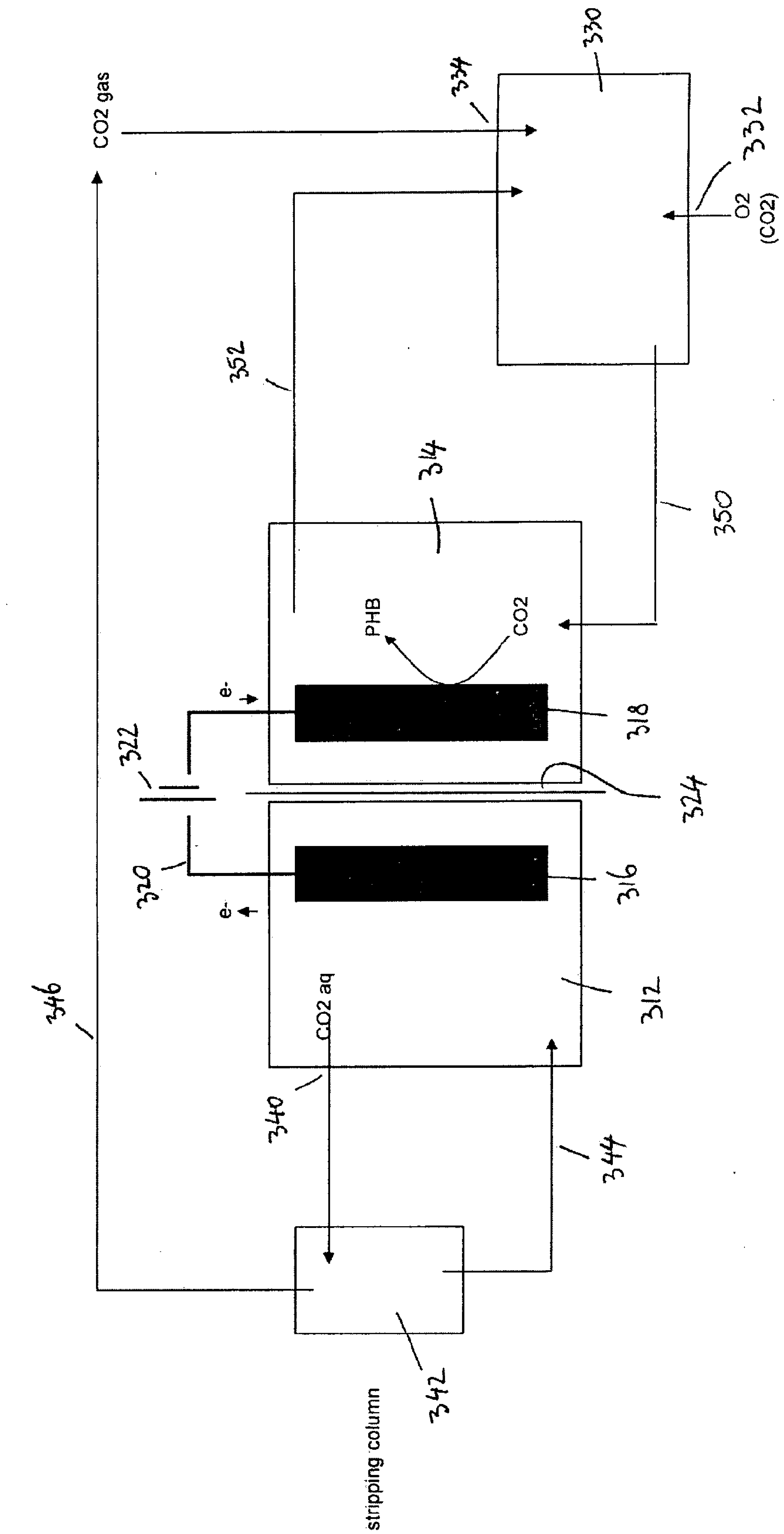
CO2 gas
330
334
332
O2
(CO2)
352
314
350
PHB
CO2
e-
322
318
324
320
316
e-
CO2 aq
346
312
340
344
342
stripping column

FIGURE 4

PROCESS FOR THE PRODUCTION OF CHEMICALS

FIELD OF THE INVENTION

[0001] The present invention relates to a process for producing chemicals. More particularly, the present invention relates to a process for producing chemicals using bioelectrochemical systems.

BACKGROUND

[0002] The global depletion of fossil fuel resources and the increasing awareness of the possible anthropogenic effect on climate change are leading to an increasing drive to reduce greenhouse gas emissions and to develop a more sustainable society. Besides renewable electricity, such a sustainable society also needs access to renewably produced fuels and chemicals. To be truly renewable these chemicals need to be produced from renewable raw materials such as biomass or from waste products such wastewater and/or carbon dioxide.

[0003] Recently, bioelectrochemical systems, such as microbial fuel cells and microbial electrolysis cells, have emerged as potentially interesting technology for the production of energy and products. Bioelectrochemical systems are based on the use of electrochemically active microorganisms, which can either donate electrons to an anode or accept electrons from a cathode. If electrochemically active micro-organisms are electrochemically interacting with an anode, such an electrode is referred to as a biological anode, bioanode or microbial bioanode. In contrast, if electrochemically active micro-organisms are electrochemically interacting with a cathode, such an electrode is referred to as a biological cathode, biocathode or microbial biocathode. Bioelectrochemical systems are generally regarded as a promising future technology for the production of energy from organic material present from aqueous waste streams (e.g., wastewater). (Rozendal et al., Trends Biotechnol. 2008, 26, 450-459). Industrial, agricultural and domestic waste waters typically contain dissolved organics that require removal before discharge into the environment. Typically, these organic pollutants are removed by aerobic treatment, which can consume large amounts of electrical energy for aeration. Bioelectrochemical wastewater treatment can be accomplished by electrically coupling a microbial bioanode to a counter electrode (cathode) that performs a reduction reaction. As a result of this electrical connection between the anode and the cathode, the electrode reactions can occur and electrons can flow from the anode to the cathode. Moreover, the electrochemically active microorganisms at the anode transfer electrons to an electrode (anode) while they are oxidising (and thus removing) (in)organic pollutants in aqueous waste streams (e.g., wastewater). A bioelectrochemical system may operate as a fuel cell (in which case electrical energy is produced—e.g. Rabaey and Verstraete, Trends Biotechnol. 2005, 23, 291-298) or as an electrolysis cell (in which case, electrical energy is fed to the bioelectrochemical system—e.g., Patent WO2005005981A2).

[0004] In 2003, Rozendal and Buisman patented biocatalysed electrolysis, which is a bioelectrochemical system for the production of hydrogen gas from bio-oxidisable material (WO 2005005981, the entire contents of which are herein incorporated by cross-reference). The bio-oxisable material used for biocatalysed electrolysis can, for example, be dissolved organic material in wastewater. In their invention Rozendal and Buisman introduced bio-oxisable material into a reactor provided with an anode and a cathode and containing anodophilic bacteria in an aqueous medium, applied a potential between the anode and cathode of between 0.1 and 1.5 volt, while maintaining a pH of between 3 and 9 in the aqueous medium and collected hydrogen gas from the cathode.

[0005] Although hydrogen is an interesting chemical to produce in a cathode, it would be even more interesting if chemicals with higher value could be produced, such as fuels and chemicals. Examples of such fuels and chemicals include alcohols such as methanol, ethanol, propanol, butanol, etc, carboxylic acids, such as formic acid, acetic acid, propionic acid, butyric acid, lactic acid, etc, biopolymers such as poly-β-hydroxybutyrate (PHB), etc., etc. However, to be able to catalyze these kind complex production reactions at a cathode, an advanced catalysis mechanism is required. It might be possible to develop chemical catalysts for this purpose, but these chemical catalysts are likely to become very complex and highly expensive as they likely necessitate the application of precious metals. Alternatively, cathodophilic microorganisms can be used for catalyzing cathodic reactions for the production of valuable chemicals. Cathodophilic microorganisms are microorganisms that can interact with a cathode by accepting electrons or cathodic reaction products (such as hydrogen or reduced electron mediators) from the cathode and utilizing these for the production of valuable chemicals. Such electrode is referred to as a biological cathode, biocathode or microbial biocathode. Electrons and cathodic reaction products (such as hydrogen or reduced electron mediators) are commonly referred to as reducing equivalents. Reducing equivalents allow reducing electron acceptors and can serve as electron donor for a microbial metabolism. Electron mediators are redox-active organic compounds and are known to person skilled in the art. They include compounds such as quinones, neutral red, methyl viologen, etc. Electron mediators shuttle in between the electrode and the microorganisms. During this shuttling the electron mediators are continuously reduced by the electrode and subsequently oxidized again by the microorganism for the production of the chemical products.

[0006] Microbial biocathodes have already been demonstrated for oxygen reduction (e.g., Rabaey et al., ISME J. 2008, 2, 1387-1396), nitrate reduction (e.g., Clauwaert et al., Environ. Sci. Technol., 2007, 41, 7564-7569), dechlorination (e.g., Aulenta et al., Environ. Sci. Technol., 2007, 41, 2554-2559), hydrogen production (e.g., Rozendal et al., Environ. Sci. Technol., 2008, 42, 629-634), and methane production (e.g., Clauwaert et al., Water Sci. Technol., 2008, 57, 575-579), but have not been described for the production of more complex molecules such as those described above.

[0007] In general, mixed microbial cultures (i.e., multiple species) are unlikely to produce complex chemicals in high quantity, concentration or purity, because the natural end products in a mixed microbial culture are typically simple molecules such as methane under anaerobic conditions or carbon dioxide under aerobic conditions. In practice, complex molecules are therefore typically produced with a defined microbial culture, such as a pure microbial culture (i.e., single specie) or at least a well-defined co-culture (i.e., two or more carefully selected species). Therefore, unless methanogenic activity can be suppressed, a microbial biocathode capable of producing complex molecules would also require a defined microbial culture of cathodophilic microorganisms (Rozendal et al., Trends Biotechnol. 2008, 26, 450-459), which are unlikely to be naturally enriched from complex inocula such as wastewater. A defined microbial culture of cathodophilic microorganisms should be a carefully selected or genetically engineered pure culture, but could also be a carefully selected co-culture of two or more carefully selected or genetically engineered pure cultures. These pure cultures or co-cultures should consist of microbial species that are capable of catalyzing the production reaction of the desired complex molecule.

[0008] A disadvantage of using a defined culture of cathodophilic microorganisms is that these cultures are susceptible to contamination with other microorganisms. So unless the activity of these other micro-organisms can be suppressed, these other microorganisms will break down the products produced by the defined culture of cathodophilic microorganisms and consequently limit the product output of the bioelectrochemical system. Bioelectrochemical systems can prevent this contamination with other micro-organisms by applying an ion exchange membrane between the anode and the cathode. The application of an ion exchange membrane isolates the cathode from the rest the bioelectrochemical system and can make the defined culture of cathodophilic microorganisms less susceptible to contamination. Even more so, because the reducing equivalents are essentially delivered to cathodophilic microorganisms sterile in the form of electrons delivered by the cathode and originally coming from the anode.

[0009] In the context of microbial fuel cells, Torres et al. (Torres et al., Environ. Sci. Technol., 2008, 42, 8773-8777) presented a method to decrease the pH difference between the anode and the cathode of a microbial fuel cell by having an anion exchange membrane between the cathode chamber and dosing carbon dioxide to an air cathode (platinum catalyst for oxygen reduction). This carbon dioxide reacts with the hydroxyl ions and forms carbonate species. While this decreases the pH of the cathode, the carbonate species also migrate across the anion exchange membrane from cathode to anode and increase pH in the latter. As a result, the pH difference between both is decreased.

BRIEF DESCRIPTION OF THE INVENTION

[0010] In a first aspect, the present invention provides a process for producing one or more chemical compounds comprising the steps of providing a bioelectrochemical system having an anode and a cathode separated by a membrane, the anode and the cathode being electrically connected to each other, causing oxidation to occur at the anode and causing reduction to occur at the cathode to thereby produce reducing equivalents at the cathode, providing the reducing equivalents to a culture of microorganisms, and providing carbon dioxide to the culture of microorganisms, whereby the microorganisms produce the one or more chemical compounds, and recovering the one or chemical compounds.

[0011] In another aspect, the present invention provides a process for producing one or more chemical compounds comprising the steps of providing a bioelectrochemical system having an anode and a cathode separated by a membrane, the anode and the cathode being electrically connected to each other, the system having a cathode compartment and the cathode compartment being provided with microorganisms that form the one or more chemical compounds in the cathode compartment, causing oxidation to occur at the anode and causing reduction to occur at the cathode, wherein carbon dioxide is supplied to the cathode compartment, and the microorganisms produce the one or more chemical compounds, and recovering the one more chemicals from the cathode compartment.

[0012] In some embodiments, the system further includes a power supply in the electrical circuit. The power supply may comprise a DC power supply, such as a battery or a DC to AC converter.

[0013] The power supply can be used to apply a voltage on the system, which increases chemical production rates. The voltage applied with a power supply between the anode and the cathode may be between 0 and 10 V, preferably between 0 and 1.5 V, more preferably between 0 and 1.0 V. This may result in a volumetric current density in the bioelectrochemical cell of between 0 and 10,000 A/m^3 of bioelectrochemical cell, preferably between 10 and 5,000 A/m^3 of bioelectrochemical cell, more preferably between 100 and 2500 A/m^3 of bioelectrochemical cell and/or an area specific current density of between 0 and 1,000 A/m^2 membrane surface area, preferably between 1 and 100 A/m^2 membrane surface area, more preferably between 2 and 25 A/m^2 membrane surface area.

[0014] In embodiments of the present invention, the microorganisms present in the cathode compartment or receiving reducing equivalents from the cathode compartment utilise reducing equivalents produced at the cathode and carbon dioxide to make organic molecules. Therefore, the carbon dioxide acts as a carbon-containing feed material to the microorganisms that receive reducing equivalents from the cathode or are present in the cathode compartment. Indeed, the carbon dioxide can be the only carbon-containing feed component supplied to the microorganisms. In other embodiments, the carbon dioxide is used in conjunction with other organic materials by the microorganisms to produce the desired chemicals. Examples of suitable microorganisms in this regard include chemolithoautotrophic bacteria. For example, in butanol formation, chemolithoautotrophic bacteria at the cathode would proceed according to:

$$4CO_2+24H^++24e^-\rightarrow C_4H_9OH+7H_2O \quad (2)$$

[0015] It will be appreciated that utilising carbon dioxide as a carbon-containing material for conversion into the desired chemical products has the desirable effect of reducing carbon dioxide emissions (and hence reducing greenhouse gas emissions).

[0016] In one embodiment, the microorganisms provided to the cathode compartment or receiving reducing equivalents from the cathode compartment comprise a defined microbial culture containing one or more selected microbial species. In one embodiment, the defined microbial culture comprises a pure microbial culture containing a single species of microorganisms. In another embodiment, the defined microbial culture comprises a co-culture of two or more carefully selected microbial species. The microbial species are selected such that the one or more chemical compounds are produced by the microbial species. Suitably, the microbial species do not form methane in notable quantities when grown in the cathode.

[0017] The defined microbial culture containing one or more selected microbial species may be formed or selected by any technique known to be suitable to persons skilled in the art.

[0018] In this embodiment, an essentially "pure" microbial culture is provided (either in the cathode compartment or to receive reducing equivalents from the cathode). The essentially "pure" microbial culture is selected such that the microbial culture produces the one or more desired chemical compounds. For example, *Clostridium carboxidivorans* sp. nov. could be selected for the production of acetate, ethanol, butyrate and butanol from carbon dioxide and cathodically produced hydrogen (Liou et al., Int. J. Syst. Evol. Microbiol., 2005, 55, 2085-2091). In order to ensure that the essentially pure microbial culture remains essentially pure, any feed streams to the culture of microorganisms should be essentially free of other microorganisms. For example, the carbon dioxide stream fed to the culture of microorganisms should also free of contaminating microorganisms.

[0019] The carbon dioxide stream being fed to be cathode compartment may be derived from an offgas stream or a flue gas stream from a burner or a boiler. It will be appreciated that such offgas streams or flue gas streams exit the burner or boiler at a very high temperature and, as a result, will be essentially sterile (in that they will not contain any contaminating microorganisms). These streams may simply be cooled and then used as a carbon dioxide containing feed stream to the cathode compartment. If the offgas stream or flue gas stream contains other material that may be toxic to the microorganisms in the cathode compartment, that other material should be removed therefrom prior to feeding to the cathode compartment. It will be appreciated that only part of the offgas stream or flue gas stream may be fed to the cathode compartment.

[0020] The carbon dioxide stream being fed to the cathode compartment may also be biogas, containing a mixture of methane and carbon dioxide (and potentially other gases)

[0021] The carbon dioxide being fed to the cathode may also be derived from a coal seam or layer, in which carbonate rich fluid is pumped from the coal seam through the cathode compartment.

[0022] In another embodiment, the microorganisms provided to the cathode compartment comprised a mixed, non-selected culture and the process further comprises the steps of producing the one or more chemicals in the cathode compartment and recovering the one or more chemicals from the cathode compartment whilst suppressing formation of methane in the cathode compartment. Persons skilled in the art will understand that mixed, non-selected cultures typically contain methanogenic organisms and, if the cathode compartment is operated without special precautions, the final product from the cathode compartment is likely to be methane. Therefore, in this embodiment, the cathode compartment is operated such that methane formation is suppressed. Methane formation may be suppressed by one or more of the following:

[0023] Adding one or more chemicals to the cathode compartment that suppress the formation of methane or suppress the activity of the methanogenic organisms. For example, 2-bromoethane sulfonate (BES) is known to suppress the activity of methanogenic organisms. Other chemicals that suppress the activity of methanogenic organisms may also be used.

[0024] Operate the cathode compartment such that a low residence time is used in the cathode compartment. In this regard, most methanogenic organisms are slow growing and utilising a low residence time in the cathode compartment will suppress the formation or growth of a significant number of methanogenic organisms in the cathode compartment because they simply will not have sufficient time to grow in any great number. In this embodiment, fresh cathode compartment liquid may be frequently or continuously provided to the cathode compartment.

[0025] Operate the cathode compartment at low pH, such as below 5.5, preferably below pH 5.

[0026] Periodically expose the cathode compartment to air or oxygen.

[0027] In one embodiment, the CO_2 is provided to the cathode compartment via diffusion or transport from the anode of the bioelectrochemical system. This transport can occur either through the membrane separating anode and cathode, or via an additional conduit.

[0028] In one embodiment, the present invention may be operated with a bioanode and a biocathode. In embodiments where the anode is operated as a bioanode, one of the products likely to be formed in the bioanode compartment is carbon dioxide. This carbon dioxide may be used as a feed to the cathode compartment. This carbon dioxide can for example separated from the anode effluent and subsequently transported to the cathode.

[0029] In embodiments where the anode is Operated as a bioanode, a waste stream, such as a wastewater stream, may be used as a feed material to the anode. The anode reaction is then catalyzed by microorganisms, such as electrochemically active microorganisms, and generates electrons (e^-) and protons and/or carbon dioxide and/or other oxidation products (e.g. sulfur):

$$\text{(In)organic materials} \rightarrow x\text{HCO}_3^- + y\text{H}^+ + ze^- + \text{other products} \quad (3)$$

[0030] The anode may be located in an anode compartment, with the anode compartment being separated from the cathode compartment by a membrane. In the anode compartment, organic and/or inorganic components in the waste stream are oxidised to liberate electrons which, in turn, flow through the electrical connection to the cathode.

[0031] In one embodiment, an anion exchange membrane separates the anode compartment from the cathode compartment. Anion exchange membranes are known to the person skilled in the art and include membranes such as AMI-7001 (Membranes International), Neosepta AMX (ASTOM Corporation), and fumasep FAA® (fumatech).

[0032] In some embodiments, bicarbonate ions form in the cathode compartment and subsequently move through the anion exchange membrane to the anode compartment. This may be advantageous in that pH control in the cathode compartment is also obtained by adding carbon dioxide to the cathode compartment. In this embodiment, the carbon dioxide acts as a feed material as a building block for producing the chemical compounds and also acts to control pH in the cathode compartment. It will be understood that hydroxyl ions can be generated by the reactions occurring at the cathode. The hydroxyl ions can react with the carbon dioxide to form bicarbonate ions and the bicarbonate ions can subsequently pass through the anion exchange membrane. In this fashion, an undesirable increase in pH in the cathode compartment (which has the potential to kill the culture of microorganisms) can be avoided and homeostatic conditions can be maintained in the cathode compartment. Carbon dioxide dosing does not significantly increase salt concentrations in the cathode compartment. This is advantageous as it will mean that a homeostatic situation can be achieved in the bioelectrochemical system.

[0033] In another embodiment, the membrane separating the anode and the cathode comprises a porous membrane. The porous membrane may allow liquid and ions to pass therethrough but prevent microorganisms from passing therethrough. In one embodiment, the anode may be operated as a bioanode, and a waste stream, such as a wastewater stream may be used as a feed material to the anode. As mentioned above, the pore size in the porous membrane may be small enough to prevent microorganisms from passing through the membrane. These membranes are known to the person skilled in the art and include microfiltration and ultrafiltration membranes. During normal operation liquid passes through the porous membrane from the anode into the cathode chamber. The protons that are generated in the anode reaction equation (3) are transported through the membrane to the cathode compartment and react with the hydroxyl ions generated in the cathode reaction in accordance with equation (4):

$$H^{+}+OH^{-}\rightarrow H_2O \quad (4)$$

[0034] As a result, an undesirable increase in the pH in the cathode compartment is avoided and no acid needs to be dosed in the cathode compartment. The pH and salt concentration in the cathode chamber remain stable and homeostasis is maintained. Dissolved or gaseous CO_2 can be transferred from the anode to the cathode alongside with the fluid.

[0035] In yet another one embodiment, the present invention may be operated with a biocathode only. In this embodiment, the anode may comprise an essentially conventional anode. In this embodiment an acid solution (e.g. sulfuric acid) may be provided to the anode compartment and the anode reaction may be a proton generating reaction (e.g. oxygen generation from water). The membrane may comprise a cation exchange membrane. Cation exchange membranes are known to the person skilled in the art and include membranes such as CMI-7000 (Membranes International), Neosepta CMX (ASTOM Corporation), Fumasep® FKB (Fumatech), and Nafion (DuPont). In this embodiment protons migrate through the cation exchange membrane and react with the hydroxyl ions generated in the cathode reaction. As a result, no acid needs to be dosed in the cathode compartment the pH and salt concentration in the cathode chamber remain stable and homeostasis is maintained.

[0036] In yet another embodiment, the electrical current used to provide the reduction in the cathode is derived from a photo-anode. Photo-anodes are known to persons skilled in the art and capture sunlight and transfers the reducing power to the electrical circuit.

[0037] In yet another embodiment, the electrical current provided to drive the biochemicals production is derived from a renewable power source such as solar power, hydro-power, or others as known to a person skilled in the art.

[0038] In yet another embodiment, the membrane separating the anode and the cathode comprises a bipolar membrane. Bipolar membranes are known to persons skilled in the art and include membranes such as NEOSEPTA BP-1E (ASTOM Corporation) and Fumasep® FBM (Fumasep). Bipolar membranes are composed of a cation exchange layer on top of an anion exchange layer and rely on the principle of water splitting into protons and hydroxyl ions in between the ion exchange layers of the membrane, according to equation (5):

$$H_2O\rightarrow H^{+}+OH^{-} \quad (5)$$

[0039] In embodiments where a bipolar membrane is used as the membrane in the bioelectrochemical system, the anion exchange layer is directed towards the anode chamber and the cation exchange layer is directed towards the cathode chamber. When electrical current flows, water diffuses in between the ion exchange layers of the bipolar membrane and is split into protons and hydroxyl ions. The hydroxyl ions migrate through the anion exchange layer into the anode chamber, where they compensate for the proton production in the anode reaction equation (3) and the protons migrate through the cation exchange layer into the cathode chamber where they compensate for the hydroxyl ion production (or proton consumption) in the cathode reaction. As a result, no acid needs to be dosed in the cathode compartment and the pH and salt concentration in the cathode chamber remain stable, maintaining homeostasis.

[0040] In another embodiment of the present invention, the effluent of the anode may be sent to, for example, a stripping column or membrane unit to recover gaseous carbon dioxide. This carbon dioxide can be provided to the cathode as a gas.

[0041] In a variation of the above embodiment effluent from the anode can be passed through a membrane unit to allow separation of carbon dioxide from the anode effluent, the membrane unit having a liquid flow on the other side of the membrane. In this manner, the separated carbon dioxide can go into solution in the fluid on the other side of the membrane. The carbon dioxide can be provided to the cathode in dissolved form. The fluid passing through the membrane unit on the other side of the anode fluid can be cathode fluid.

[0042] In another embodiment, the anode effluent can be sent through a membrane unit to allow carbon dioxide together with organic constituents of the anode effluent to pass to a second liquid. For example, effluents from fermentation reactors can be sent through an anode, the effluent of the anode can be sent to a membrane unit where aside from the carbon dioxide fatty acids such as propionate, butyrate and others as known to a person skilled in the art pass through the membrane and become captured in a second fluid. This fluid can be sent to the cathode where reduction of the organics can occur. In this embodiment, both carbon dioxide and the other organic materials provide feed material for the microorganisms to convert into the desired chemical products.

[0043] In one embodiment, the cathode is also provided with organic molecules to assist in the production of the biochemicals. Examples of such organic molecules are glycerol, glucose, lactate, butyrate, and others known to a person skilled in the art. These compounds can be added to provide the microorganisms with a source for adenosyl triphosphate (ATP) formation, which facilitates microbial growth and product formation.

[0044] In the case of glycerol addition, the product formation may include 1,3-propanediol or butanol. Glycerol may be added to the cathode compartment, to the anode compartment or to both. Glycerol can also be (partially) converted to propionate prior to entry in the bioelectrochemical system, and subsequently be added to the cathode as a mixture of glycerol and propionate.

[0045] In one embodiment, the microorganisms in the cathode compartment are genetically engineered to receive electrons from the cathode. Examples of modifications include the addition of hydrogenases, cytochromes, sortases and other enzyme complexes to the cell. Alternatively, the cathode can be provided with conductive structures, such as nanowires, to electrically connect microorganisms with the cathode.

[0046] In another embodiment, redox mediators can be added to the cathode fluid, allowing transport of electrons from the cathode to the microorganism. Examples of redox mediators are methyl viologen, neutral red, phenazine carboxamide, amido black and others as known to a person skilled in the art. The redox shuttles allow in certain embodiments to increase the ratio $NADH/NAD^+$ inside the microbial cell, which drives the production of reduced molecules.

[0047] In some embodiments of the process of the present invention, a mixture of desirable chemicals may be formed in the cathode compartment. In such embodiments, the present invention further comprises the steps of removing a mixture of chemical compounds from the cathode compartment and separating the mixture of chemical compounds into two or more streams. The mixture of chemical compounds may be separated using known separation techniques, such as ion exchange, liquid-liquid extraction, absorption, absorption, gas stripping, distillation, reverse osmosis, membrane separation, cryogenic separation, or indeed any other separation technique known to be suitable to a person skilled in the art. In some embodiments, one or more of the chemical compounds may be reacted to form another chemical compound that is more susceptible to removal from the remaining chemical compounds. In some embodiments, one or more of the chemical compounds formed in the cathode compartment may comprise a solid compound. In such embodiments, any suitable solid/liquid separation technique may be used, including centrifugation, filtration, settling, clarification, flotation, or the like. In other embodiments, one or more of the chemical compounds formed in the cathode compartment may comprise a gaseous compound. In such embodiments, product can conveniently be collected with a gas collection device, such as a gas-liquid separator, as known to a person skilled in the art.

[0048] In some embodiments of the present invention, the cathode compartment is filled with the microbial culture. The microbial culture is typically part of an aqueous mixture in the cathode compartment. In other embodiments of the present invention, the microbial culture grows on the electrode surface. In yet other embodiments of the present invention, the cathode compartment is filled with part of the microbial culture and another part of the microbial culture grows on the electrode surface.

[0049] In some embodiments of the present invention, the cathode compartment may comprise a first compartment housing the cathode, the first compartment including a redox shuttle, and a second compartment containing one or more microorganisms, wherein the redox shuttle is reduced in the first compartment and a reduced redox shuttle is provided to the second compartment, the second compartment containing microorganisms that use the reduced redox shuttle as an electron donor to facilitate formation of the one more chemicals. The reduced redox shuttle is converted to an oxidised redox shuttle in the second compartment. The oxidised redox shuttle may be returned to the first compartment.

[0050] Examples of chemical compounds that can be formed using the present invention include:

- **[0051]** alcohols such as methanol, ethanol, propanol, butanol, isobutanol etc.
- **[0052]** carboxylic acids, such as formic acid, acetic acid, propionic acid, butyric acid, lactic acid, etc.
- **[0053]** diols such as 1,3-propanediol and 1,2-propanediol
- **[0054]** biopolymers such as poly-β-hydroxybutyrate (PHB), etc,
- **[0055]** any other organic chemical that can be produced by micro-organisms from carbon dioxide and reducing equivalents, in the presence or absence of organic chemicals.

BRIEF DESCRIPTION OF THE DRAWINGS

[0056] FIG. **1** shows a schematic view of a bioelectrochemical system suitable for use in embodiments of the present invention;

[0057] FIG. **2** shows a schematic diagram of apparatus suitable for use in another embodiment of the present invention;

[0058] FIG. **3** shows a schematic diagram of apparatus suitable for use in a further embodiment of the present invention; and

[0059] FIG. **4** shows a schematic diagram of apparatus suitable for use in a further embodiment of the present invention.

DETAILED DESCRIPTION OF THE DRAWINGS

[0060] It will be appreciated that the drawings have been provided for the purpose of illustrating preferred embodiments of the present invention. Therefore, it will be understood that the present invention should not be considered to be limited to the features are shown in the drawings.

[0061] The bioelectrochemical system **10** shown in FIG. **1** includes an anode compartment **12** and a cathode compartment **14**. The anode compartment **12** includes an anode **16**. The cathode compartment **14** includes a cathode **18**. The anode and the cathode are in electrical connection with each other via an electrical circuit **20** that contains a power supply **22**. The anode compartment **12** is separated from the cathode compartment **14** by an anion exchange membrane **24**.

[0062] The cathode compartment **14** contains a microbial culture (shown schematically in FIG. **1** as ovals or circles **17** and **19**). In the embodiment shown in FIG. **1**, the microbial culture comprises a defined culture. A defined microbial culture of cathodophilic microorganisms should be a carefully selected or genetically engineered pure culture, but could also be a carefully selected co-culture of two or more carefully selected or genetically engineered pure cultures. These pure cultures or co-cultures should consist of microbial species that are capable of catalyzing the production reaction of the desired complex molecule. The microbial culture in the cathode compartment **14** is contained in an aqueous medium (see reference numeral **17**) and/or attached to the cathode (see reference numeral **19**).

[0063] The cathode compartment **14** is provided with a gas inlet **26** and a gas outlet **28**. A carbon dioxide containing stream is fed into the gas in **26** and excess gas is removed through gas outlet **28**. The carbon dioxide containing stream that is fed to the cathode compartment is a sterile carbon dioxide containing stream in that it contains no contaminating microorganisms. One possible source of such a carbon dioxide containing stream is an offgas stream from a boiler or a furnace. Such an offgas stream leaves the boiler or furnace that elevated temperatures and therefore contained no microorganisms (and microorganisms would be killed by the high temperatures encountered in the offgas stream). The offgas stream may be cooled (in a manner which does not introduce any contaminating bacteria into the gas stream, such as by using indirect heat exchange) and subsequently be fed to the cathode compartment **14**.

[0064] Liquid from the cathode compartment **14** circulates through liquid line **30**. Pump **32** is used to maintain this liquid circulation. A separator **34** is used to separate valuable product from the liquid and the valuable product is recovered at **36**. The nature of the separator will be determined by the valuable product(s) to be separated from the liquid. The person skilled in the art will readily appreciate how to design an appropriate separator for each product being formed.

[0065] FIG. **2** shows a schematic view of an alternative apparatus suitable for use in the present invention. The apparatus shown in FIG. **2** includes an anode compartment **112** that contains an anode **116**. The apparatus also includes a cathode compartment **114** that contains a cathode **118**. A membrane **124** separates the cathode compartment from the anode compartment. An electrical circuit **120** that includes a power supply **122** (in the form of a DC power supply, such as a battery or an AC to DC converter) electrically connects the anode **116** to cathode **118**.

[0066] The apparatus also includes a separate vessel **130**. The vessel **130** has an inlet **132** in which carbon dioxide and oxygen or an oxygen containing gas can be supplied. The oxygen and carbon dioxide can be transferred via line **134** to compartment **114**. Line **136** returns fluid and excess gas to the vessel **130**. The vessel **130** may also be provided with an aqueous medium and the carbon dioxide and oxygen may dissolve into the aqueous medium, with the aqueous medium containing dissolved carbon dioxide and oxygen being transferred to the cathode compartment **114**.

[0067] FIG. **3** shows a schematic view of another apparatus suitable for use in embodiments of the present invention. The apparatus shown in FIG. **3** includes an anode compartment **212** that contains an anode **216**. The apparatus also includes a cathode compartment **214** that contains a cathode **218**. A membrane **224** separates the cathode compartment from the anode compartment. An electrical circuit **220** that includes a power supply **222** (in the form of a DC power supply, such as a battery or an AC to DC converter) electrically connects the anode **216** to the cathode **218**.

[0068] The apparatus shown in FIG. **3** also includes a further vessel **230**. The vessel **230** has an inlet **232** for admitting carbon dioxide to the vessel **230**. In the embodiment shown in FIG. **3**, a redox shuttle is reduced in the cathode compartment **214**. The reduced redox shuttle is supplied via line **236** to the external compartment **230**. A culture of microorganisms in the vessel **230** uses the reduced redox shuttle as an electron donor for the reduction of carbon dioxide. The oxidised redox shuttle is then returned to the cathode compartment **214** via line **238**.

[0069] FIG. **4** shows a schematic view of another apparatus suitable for use in embodiments of the present invention. The apparatus shown in FIG. **4** includes an anode compartment **312** that contains an anode **316**. The apparatus also includes a cathode compartment **314** that contains a cathode **318**. A membrane **324** separates the cathode compartment from the anode compartment. An electrical circuit **320** that includes a power supply **322** electrically connects the anode **316** to cathode **318**.

[0070] The apparatus also includes a vessel **330** that has an inlet **332** for supplying oxygen (and additional carbon dioxide, if required) thereto. Line **350** transfers oxygen and carbon dioxide to the cathode compartment **314** and line **352** returns excess oxygen and carbon dioxide to vessel **330**. The oxygen and carbon dioxide may be transferred as gaseous streams or dissolved in liquid streams.

[0071] In the embodiment shown in FIG. **4**, the reaction is taking place at the anode produce carbon dioxide in the anode compartment **312**. An outlet **340** from the anode compartment removes aqueous liquid containing carbon dioxide from the anode compartment and passes it to a stripping column **342**. In the stripping column, carbon dioxide is separated from the aqueous liquid. The aqueous liquid is returned to the anode compartment **312** via line **344**. The stripped carbon dioxide is transferred via line **346** to inlet **334** of vessel **330**. The carbon dioxide and oxygen in the vessel **330** is transferred to cathode compartment **314**, where a selected culture of microorganisms converts the carbon dioxide into other chemical compounds. This embodiment is advantageous in that carbon dioxide that forms at the anode is captured and used as a feed to the cathode compartment, thereby reducing carbon dioxide emissions.

EXAMPLES

Example 1

Biopolymer Production

[0072] In this example, which uses the apparatus as shown in FIG. **2**, bacteria in the cathode chamber use carbon dioxide and electrons from the cathode as energy and carbon source, in which case they can produce biopolymer under the form of poly-β-hydroxybutyrate (PHB). The CO_2 is provided in a way that a pure culture or a defined mixture of bacteria can be maintained. Oxygen is supplied to support the PHB synthesis. The electrons reach the bacteria either directly or indirectly through e.g. the production of hydrogen at the cathode. An external power source can provide the required additional reducing power at the cathode, if required

[0073] Example organism in the cathode: *Cupriavidus necator* (formerly *Alcaligenes eutrophus* or *Ralstonia eutropha*)

Example 2

Indirect Provision of Reducing Power to Biochemicals Producing Organisms

[0074] In this example the apparatus as shown in FIG. **3** is used and a redox shuttle is reduced in the cathode compartment. The reduced redox shuttle is brought to the external compartment (possibly through a permeable membrane) where micro-organisms use the reduced redox shuttle as electron donor for the reduction of an electron acceptor, being CO_2, and the production chemicals from this CO_2. An external power source can provide the required additional reducing power at the cathode, if required

Example 3

Reuse of CO_2 Produced at the Anode to Drive the Cathodic Reaction

[0075] This example is conducted in the apparatus as shown in FIG. **4**. The anode contains micro-organisms that oxidize a carbon source. The CO_2 produced is stripped in situ, or in an external stripping reactor, and hence brought to the cathode compartment in such way that the cathode compartment can contain a well defined culture or mixed culture of micro-organisms to form the desired chemicals.

[0076] The present invention presents a cathode system for producing complex molecules using microbial biocathodes prevents the abovementioned problems associated with the contamination of unwanted micro-organisms and/or cathode chamber pH increase and/or salinity increase.

1. A process for producing one or more chemical compounds comprising the steps of providing a bioelectrochemical system having an anode and a cathode separated by a membrane, the anode and the cathode being electrically connected to each other, causing oxidation to occur at the anode and causing reduction to occur at the cathode to thereby produce reducing equivalents at the cathode, providing the reducing equivalents to a culture of microorganisms, and providing carbon dioxide to the culture of microorganisms, whereby the microorganisms produce the one or more chemical compounds, and recovering the one or chemical compounds.

2. A process as claimed in claim **1** wherein the microorganisms that form the one or more chemical compounds are present in the cathode compartment, and the process comprises causing oxidation to occur at the anode and causing reduction to occur at the cathode, wherein carbon dioxide is supplied to the cathode compartment, and the microorganisms produce the one or more chemical compounds, and recovering the one more chemicals from the cathode compartment.

3. A process as claimed in claim **1** wherein the bioelectrochemical system includes a power supply in the electrical circuit.

4. A process as claimed in claim **1** wherein the carbon dioxide acts as a carbon-containing feed material to the microorganisms that receive the reducing equivalents from the cathode or are present in the cathode compartment and the carbon dioxide comprises the only carbon-containing feed component supplied to the microorganisms.

5. A process as claimed in claim **1** wherein the carbon dioxide acts as a carbon-containing feed material to the microorganisms that receive the reducing equivalents from the cathode or are present in the cathode compartment and the carbon dioxide is used in conjunction with other organic materials by the microorganisms to produce the chemicals.

6. A process as claimed in claim **1** wherein the microorganisms provided to the cathode compartment or receiving reducing equivalents from the cathode compartment comprise a defined microbial culture containing one or more selected microbial species.

7. A process as claimed in claim **1** wherein the microbial species do not form methane in notable quantities when grown in the cathode.

8. A process as claimed in claim **1** wherein the microorganisms comprise a mixed, non-selected culture and the process further comprises the steps of producing the one or more chemicals in the cathode compartment and recovering the one or more chemicals from the cathode compartment whilst suppressing formation of methane in the cathode compartment.

9. A process as claimed in claim **8** wherein methane formation is suppressed by one or more of adding one or more chemicals to the cathode compartment that suppress the formation of methane or suppress the activity of the methanogenic organisms, operating the cathode compartment such that a low residence time is used in the cathode compartment, operating the cathode compartment at low pH, such as below 5.5, or periodically exposing the cathode compartment to air, oxygen or hydrogen peroxide.

10. A process as claimed in claim **1** wherein the bioelectrochemical system comprises a bioanode and a biocathode.

11. A process as claimed in claim **1** wherein one of the products formed in the anode compartment is carbon dioxide and this carbon dioxide is used as a feed to the cathode compartment.

12. A process as claimed in claim **1** wherein an anion exchange membrane separates the anode compartment from the cathode compartment.

13. A process as claimed in claim **12** wherein bicarbonate ions form in the cathode compartment and subsequently move through the anion exchange membrane to the anode compartment to thereby avoid increases in pH and/or salinity in the cathode compartment that could kill the microorganisms.

14. A process as claimed in claim **1** wherein the membrane separating the anode and the cathode comprises a porous membrane that allows liquid and ions to pass therethrough but prevents microorganisms from passing therethrough.

15. A process as claimed in claim **14** wherein the anode is operated as a bioanode and a waste stream is used as a feed material to the anode and during normal operation liquid passes through the porous membrane from the anode into the cathode chamber, and protons generated in an anode reaction are transported through the membrane to the cathode compartment and react with the hydroxyl ions generated in a cathode reaction in accordance with equation (4) to thereby avoid an undesirable increase in the pH in the cathode compartment:

$$H^{+}+OH^{-}\rightarrow H_2O \quad (4)$$

16. A process as claimed in claim **15** wherein pH and salt concentration in the cathode chamber remain stable and homeostasis is maintained.

17. A process as claimed in claim **1** wherein the bioelectrochemical system is operated with a biocathode only.

18. A process as claimed in claim **17** wherein an acid solution is provided to the anode compartment and the anode reaction comprises a proton generating reaction, and the membrane comprises a cation exchange membrane and protons migrate through the cation exchange membrane and react with the hydroxyl ions generated in the cathode reaction.

19. A process as claimed in claim **1** wherein the membrane separating the anode and the cathode comprises a bipolar membrane.

20. A process as claimed in claim **19** wherein the bipolar membrane is composed of a cation exchange layer on top of an anion exchange layer and the anion exchange layer is directed towards the anode chamber and the cation exchange layer is directed towards the cathode chamber such that when electrical current flows, water diffuses in between layers of the bipolar membrane and is split into protons and hydroxyl ions, and the hydroxyl ions migrate through the anion exchange layer into the anode chamber where they compensate for the proton production in the anode reaction and the protons migrate through the cation exchange layer into the cathode chamber where they compensate for hydroxyl ion production (or proton consumption) in the cathode reaction.

21. A process as claimed in claim **1** wherein the effluent of the anode contains carbon dioxide and the effluent from the anode is sent to a stripping column or membrane unit to recover gaseous carbon dioxide for supply to the cathode as a gas.

22. A process as claimed in claim **21** wherein effluent from the anode is passed through a membrane unit to allow separation of carbon dioxide from the anode effluent, the membrane unit having a liquid flow on the other side of the membrane such that the separated carbon dioxide goes into solution in the fluid on the other side of the membrane and the carbon dioxide is provided to the cathode in dissolved form.

23. A process as claimed in claim **22** wherein the fluid passing through the membrane unit on the other side of the anode fluid comprises cathode fluid.

24. A process as claimed in claim **22** wherein the anode effluent is sent through a membrane unit to allow carbon dioxide together with organic constituents of the anode effluent to pass to a second liquid and the second fluid is sent to the cathode where reduction of the organics occurs.

25. A process as claimed in claim **1** wherein a mixture of chemicals is formed in the cathode compartment and the process further comprises the steps of removing a mixture of chemical compounds from the cathode compartment and separating the mixture of chemical compounds into two or more streams.

26. A process as claimed in claim **1** wherein the cathode compartment is filled with the microbial culture and the microbial culture is part of an aqueous mixture in the cathode compartment, or the microbial culture grows on the electrode surface or the cathode compartment is filled with part of the microbial culture and another part of the microbial culture grows on the electrode surface.

27. A process as claimed in claim **1** wherein the cathode compartment comprises a first compartment housing the cathode, the first compartment including a redox shuttle, and a second compartment containing one or more microorganisms, wherein the redox shuttle is reduced in the first compartment and a reduced redox shuttle is provided to the second compartment, the second compartment containing microorganisms that use the reduced redox shuttle as an electron donor to facilitate formation of the one more chemicals.

28. A method as claimed in claim **27** wherein the reduced redox shuttle is converted to an oxidised redox shuttle in the second compartment and the oxidised redox shuttle is returned to the first compartment.

29. A process as claimed in claim **1** wherein the chemical compounds that are formed include:

alcohols such as methanol, ethanol, propanol, butanol, isobutanol

carboxylic acids, such as formic acid, acetic acid, propionic acid, butyric acid, lactic acid,

diols such as 1,3-propanediol and 1,2-propanediol,

biopolymers such as poly-β-hydroxybutyrate (PHB).

30. A process as claimed in claim **1** wherein the chemical compound being formed comprises butanol and the bioelectrochemical system includes chemolithoautotrophic bacteria at the cathode that produce butanol according to equation (2):

$$4CO_2+24H^++24e^-\rightarrow C_4H_9OH+7H_2O \quad (2)$$

31. A process as claimed in claim **1** wherein the carbon dioxide stream being fed to be cathode compartment is derived from an offgas stream or a flue gas stream from a burner or a boiler.

32. A process as claimed in claim **1** wherein a voltage is applied between the anode and the cathode of between 0 and 10 V, preferably between 0 and 1.5 V, more preferably between 0 and 1.0 V and a volumetric current density in the bioelectrochemical cell of between 0 and 10,000 A/m^3 of bioelectrochemical cell, preferably between 10 and 5,000 A/m^3 of bioelectrochemical cell, more preferably between 100 and 2500 A/m' of bioelectrochemical cell and/or an area specific current density of between 0 and 1,000 A/m^2 membrane surface area, preferably between 1 and 100 A/m^2 membrane surface area, more preferably between 2 and 25 A/m^2 membrane surface area, is obtained.

33. A process as claimed in claim **1** wherein the carbon dioxide stream being fed to the cathode compartment comprises biogas containing a mixture of methane and carbon dioxide or the carbon dioxide being fed to the cathode is be derived from a coal seam or layer, in which carbonate rich fluid is pumped from the coal seam through the cathode compartment.

34. A process as claimed in claim **1** wherein carbon dioxide is provided to the cathode compartment via diffusion or transport from the anode of the bioelectrochemical system.

35. A process as claimed in claim **1** wherein the cathode is also provided with organic molecules to assist in the production of the biochemicals.

36. A process as claimed in claim **35** wherein the organic molecules are selected from glycerol, glucose, lactate, propionate and butyrate.

37. A process as claimed in claim **36** wherein glycerol is added and product formation includes 1,3-propanediol or butanol, and glycerol is added to the cathode compartment, to the anode compartment or to both.

38. A process as claimed in claim **37** wherein the glycerol can also be partly converted to propionate prior to entry in the bioelectrochemical system, and subsequently added to the cathode as a mixture of glycerol and propionate.

39. A process as claimed in claim **1** wherein redox mediators are added to the cathode fluid, allowing transport of electrons from the cathode to the microorganism.

40. A process as claimed in claim **39** wherein the redox mediators are selected from methyl viologen, neutral red, phenazine carboxamide, amido black or mixtures of two or more thereof.

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