

(19) **United States**(12) **Patent Application Publication**  
**Oloman et al.**(10) **Pub. No.: US 2008/0223727 A1**(43) **Pub. Date: Sep. 18, 2008**(54) **CONTINUOUS CO-CURRENT  
ELECTROCHEMICAL REDUCTION OF  
CARBON DIOXIDE**(52) **U.S. Cl. .... 205/413**(76) Inventors: **Colin Oloman, Vancouver (CA);  
Hui Li, Vancouver (CA)**(57) **ABSTRACT**Correspondence Address:  
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In various embodiments, the invention provides electrochemical processes for reduction of carbon dioxide, for example converting carbon dioxide to formate salts or formic acid. In selected embodiments, operation of a continuous reactor with a three dimensional cathode and a two-phase (gas/liquid) catholyte flow provides advantageous conditions for electro-reduction of carbon dioxide. In these embodiments, the continuous two-phase flow of catholyte solvent and carbon dioxide containing gas, in selected gas/liquid phase volume flow ratios, provides dynamic conditions that favour the electro-reduction of CO<sub>2</sub> at relatively high effective superficial current densities and gas space velocities, with relatively low reactor (cell) voltages (<10 Volts). In some embodiments, relatively high internal gas hold-up in the cathode chamber (evident in an internal gas to liquid phase volume ratio >0.1) may provide greater than equilibrium CO<sub>2</sub> concentrations in the liquid phase, also facilitating relatively high effective superficial current densities. In some embodiments, these characteristics may for example be achieved at catholyte pH >7 and relatively low CO<sub>2</sub> partial pressures (<10 bar). In some embodiments, these characteristics may for example be achieved under near adiabatic conditions, with catholyte outlet temperature up to about 80° C.

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(2), (4) Date: **Apr. 11, 2008****Related U.S. Application Data**

(60) Provisional application No. 60/725,642, filed on Oct. 13, 2005.

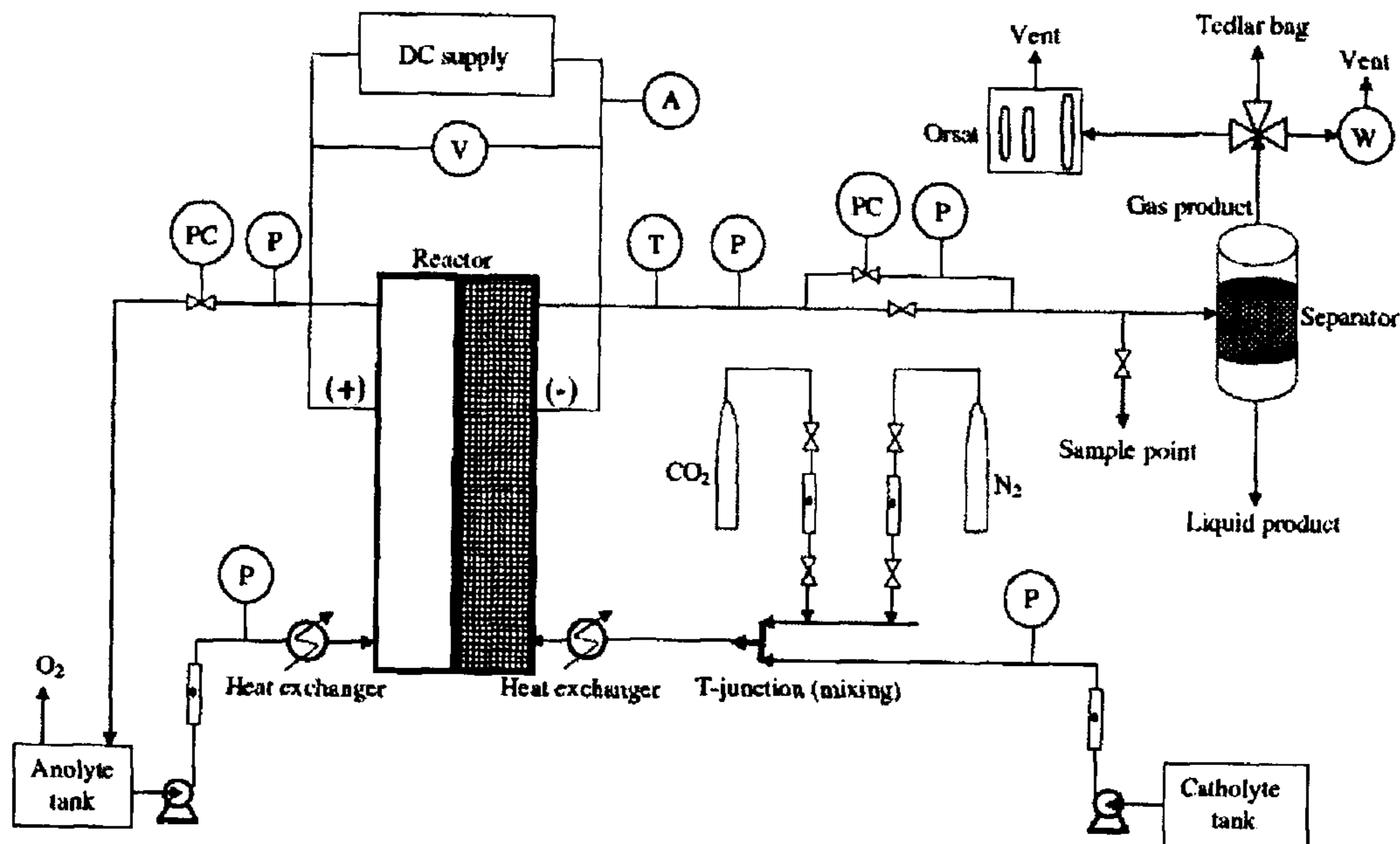
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**C25B 3/04** (2006.01)

Figure 1

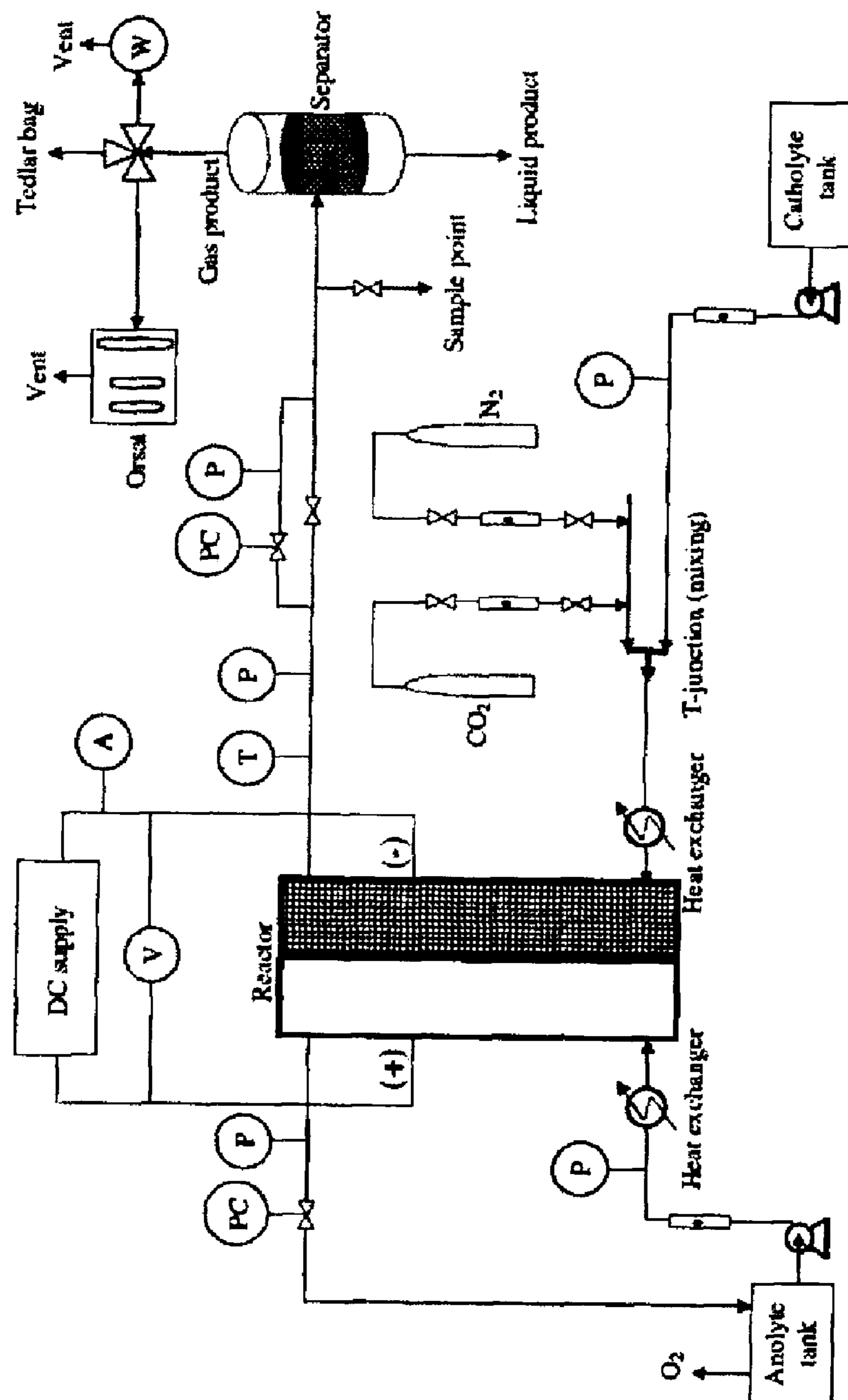


Figure 2

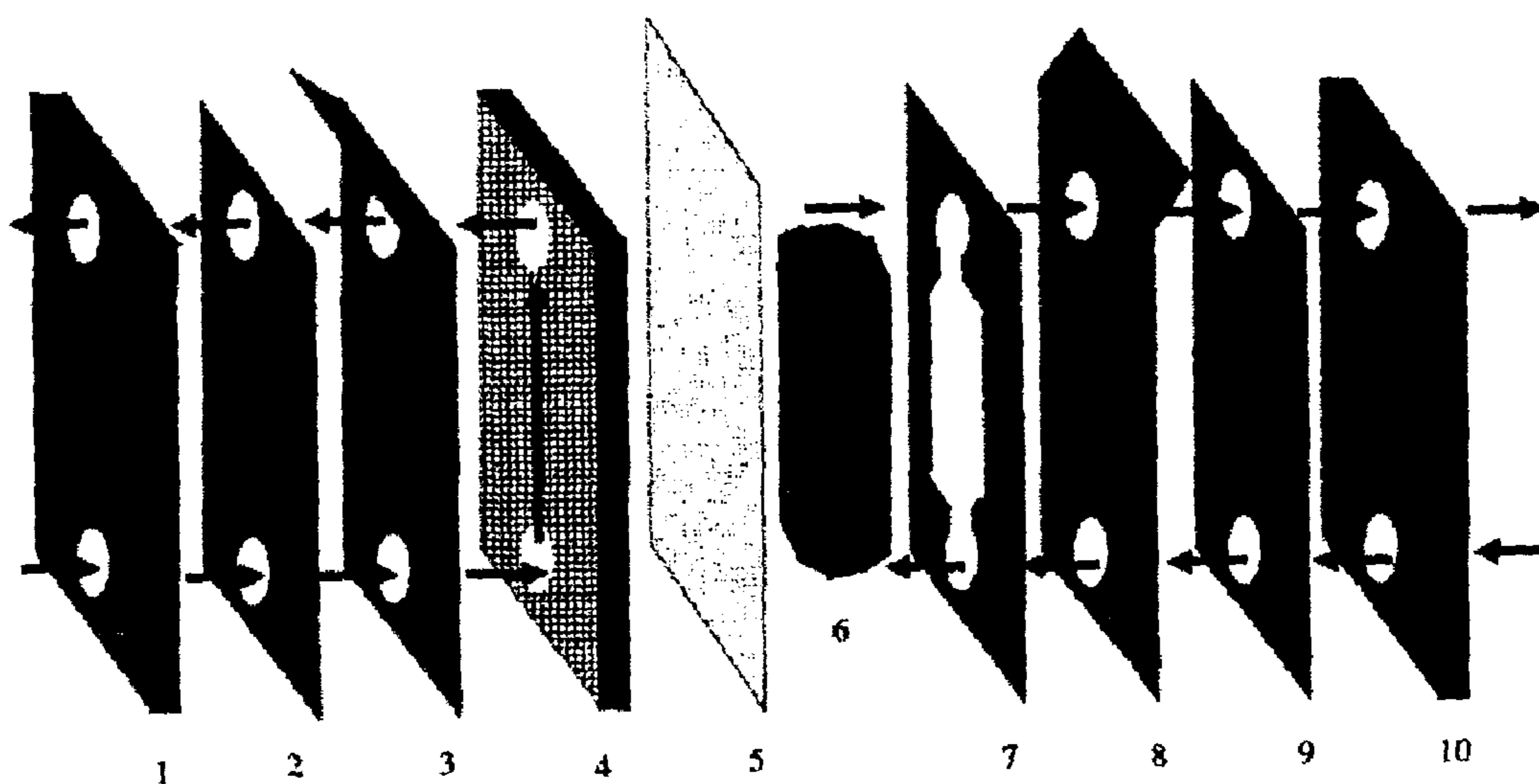


Figure 3

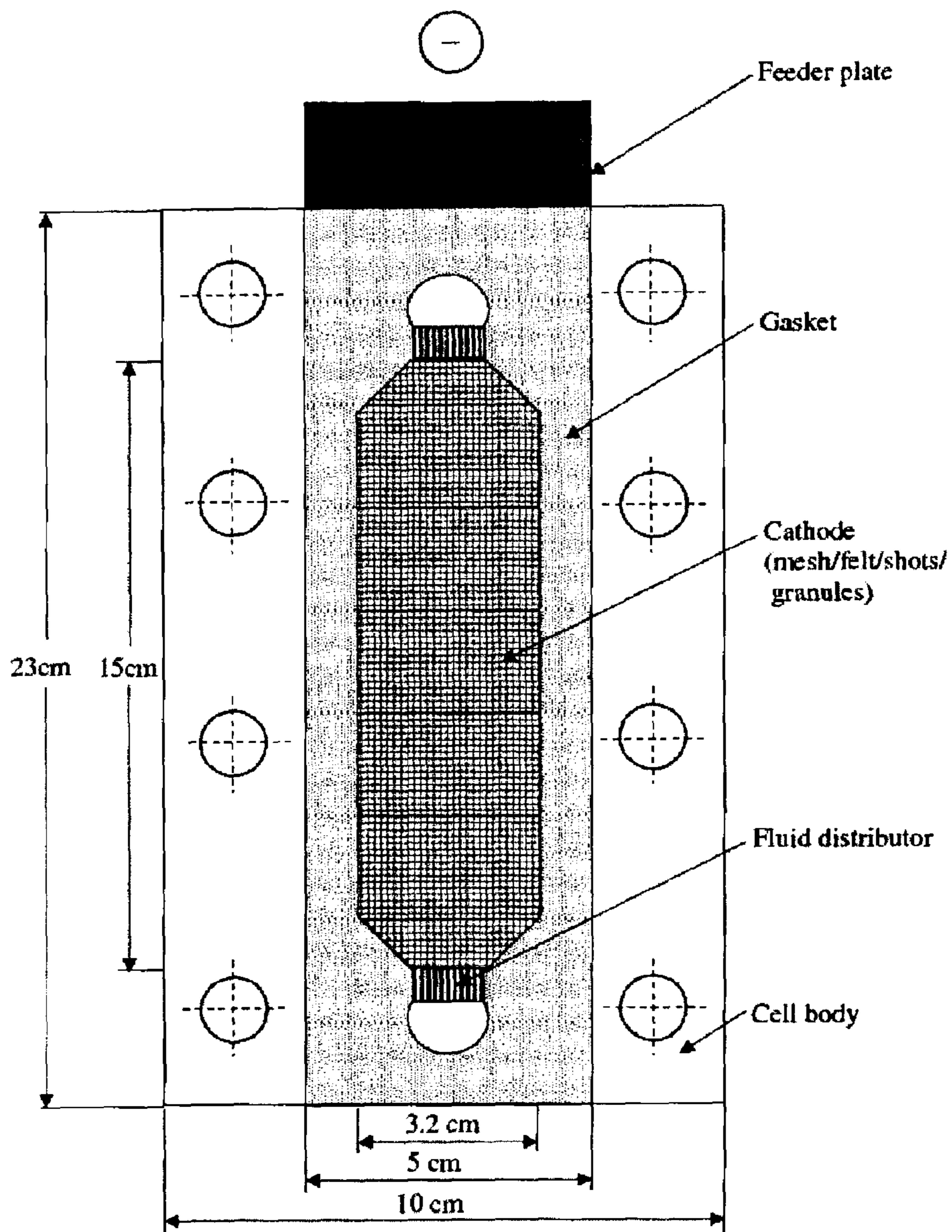


Figure 4

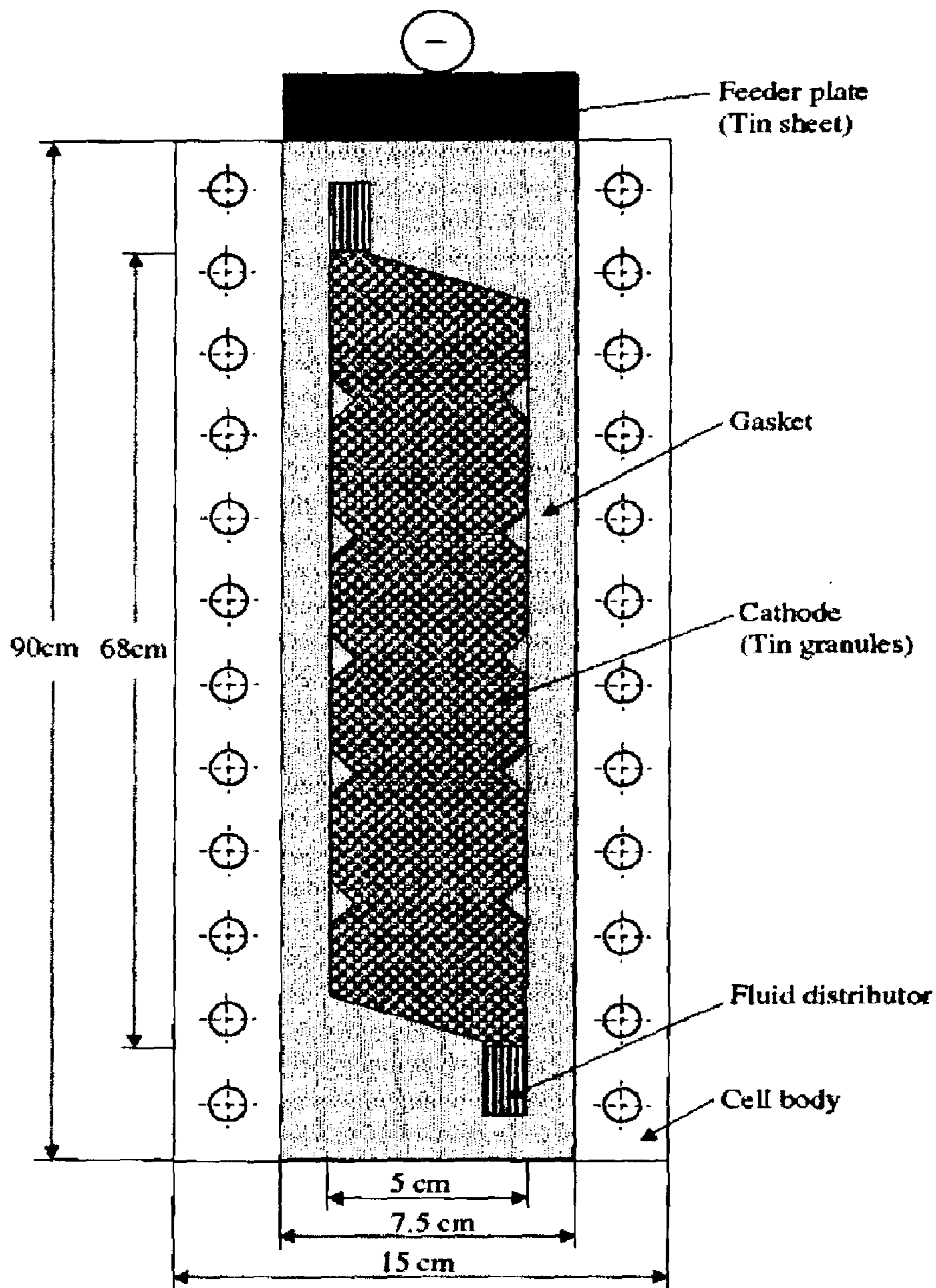


Figure 5

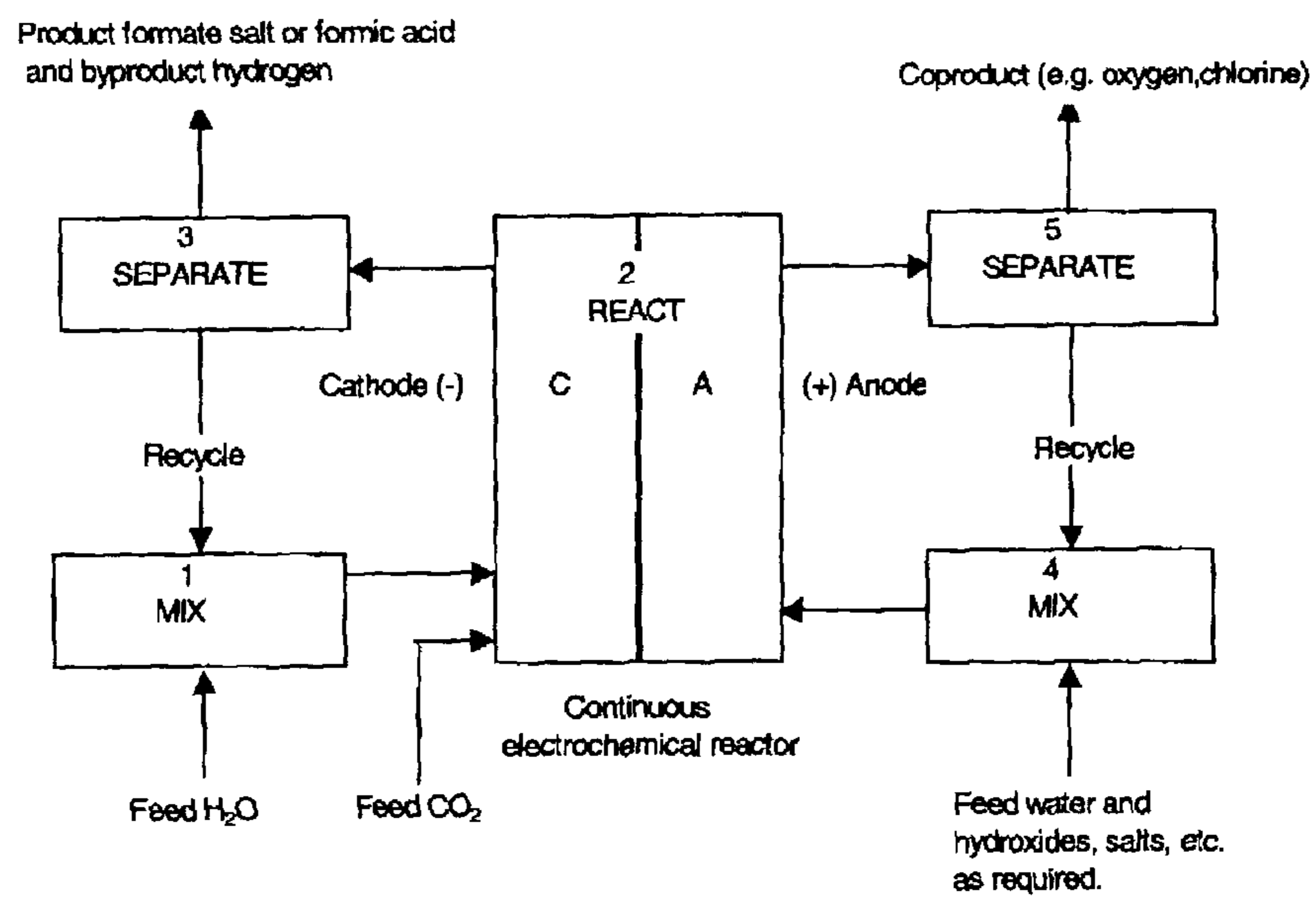


Figure 6

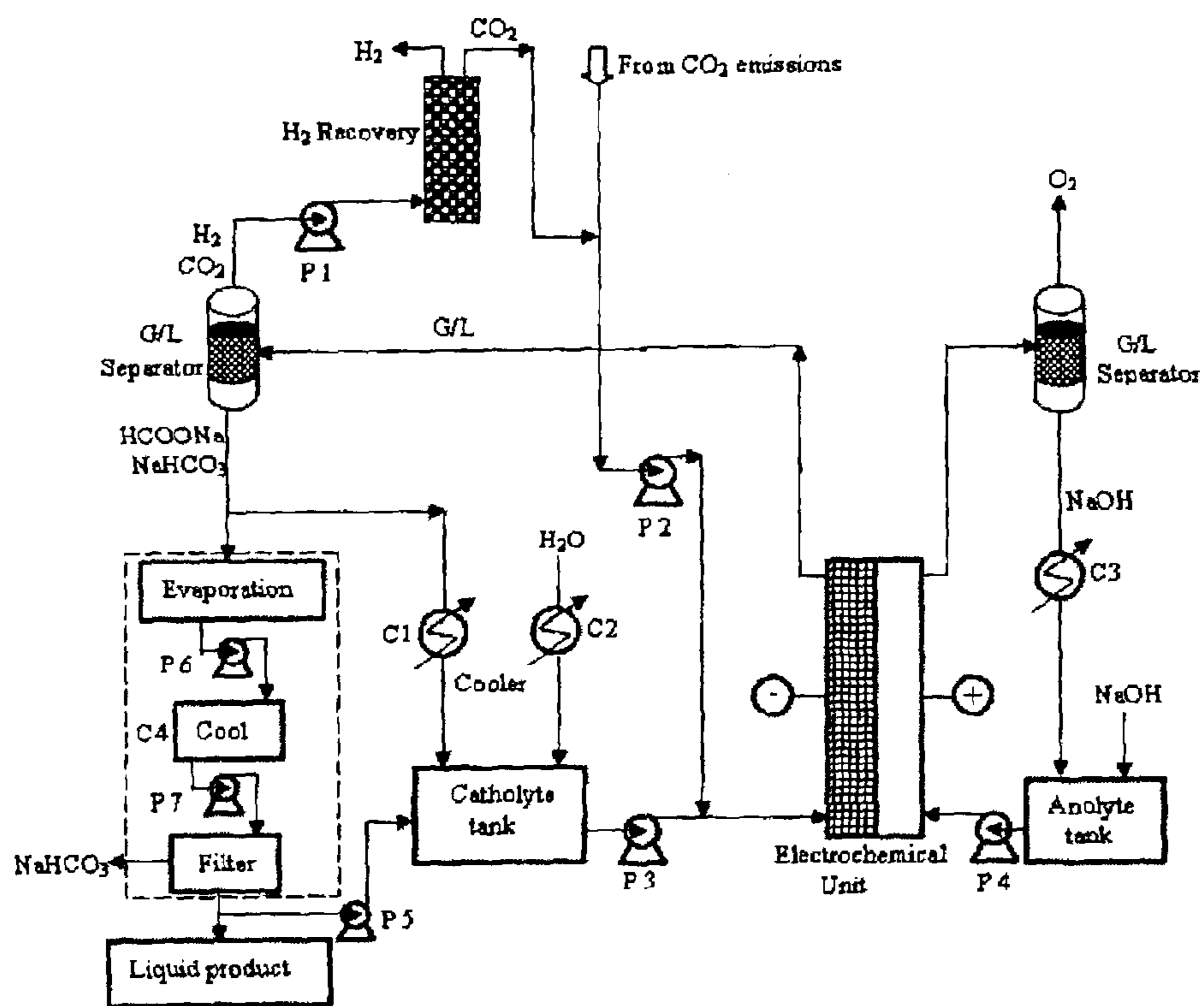


Figure 7

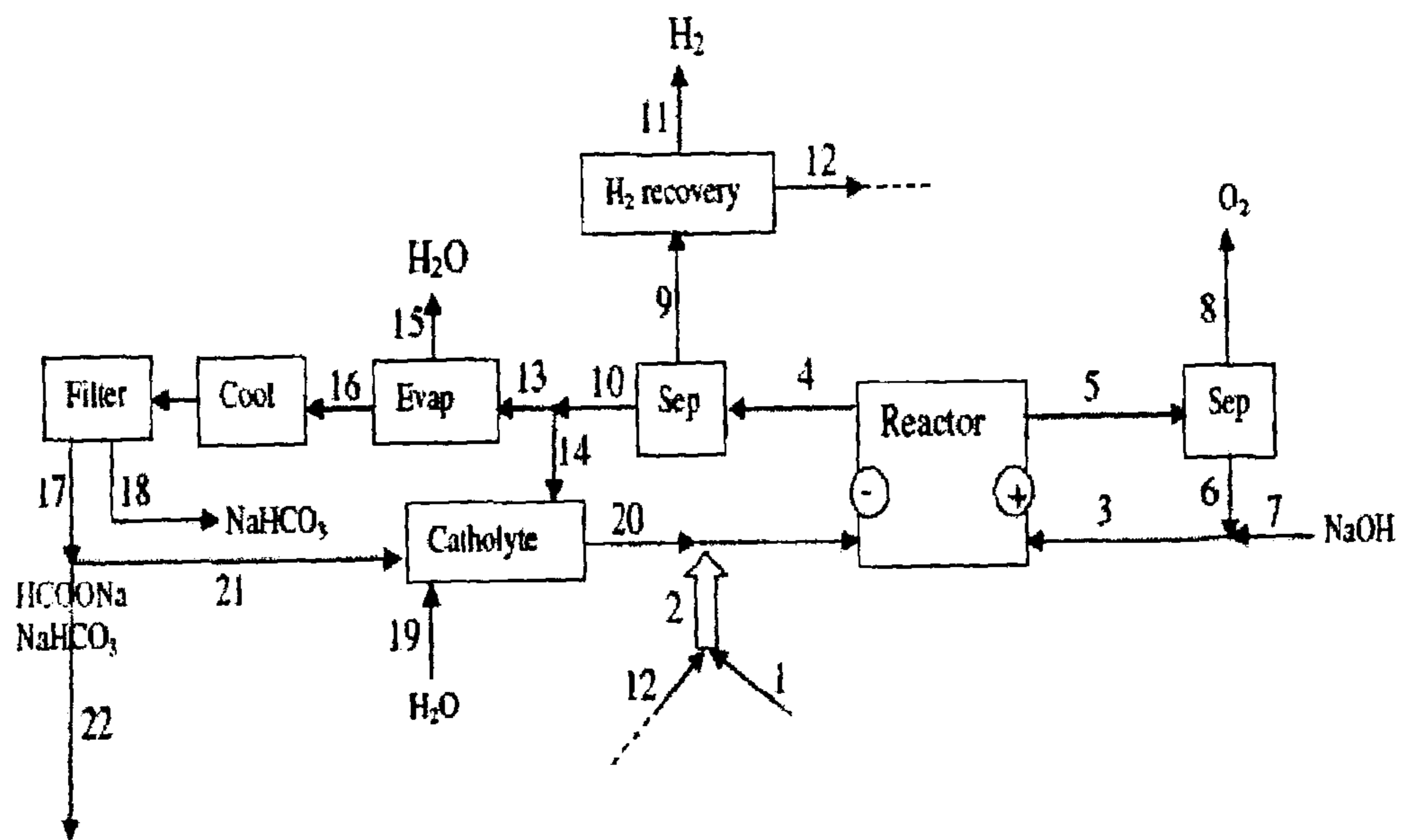




Figure 8

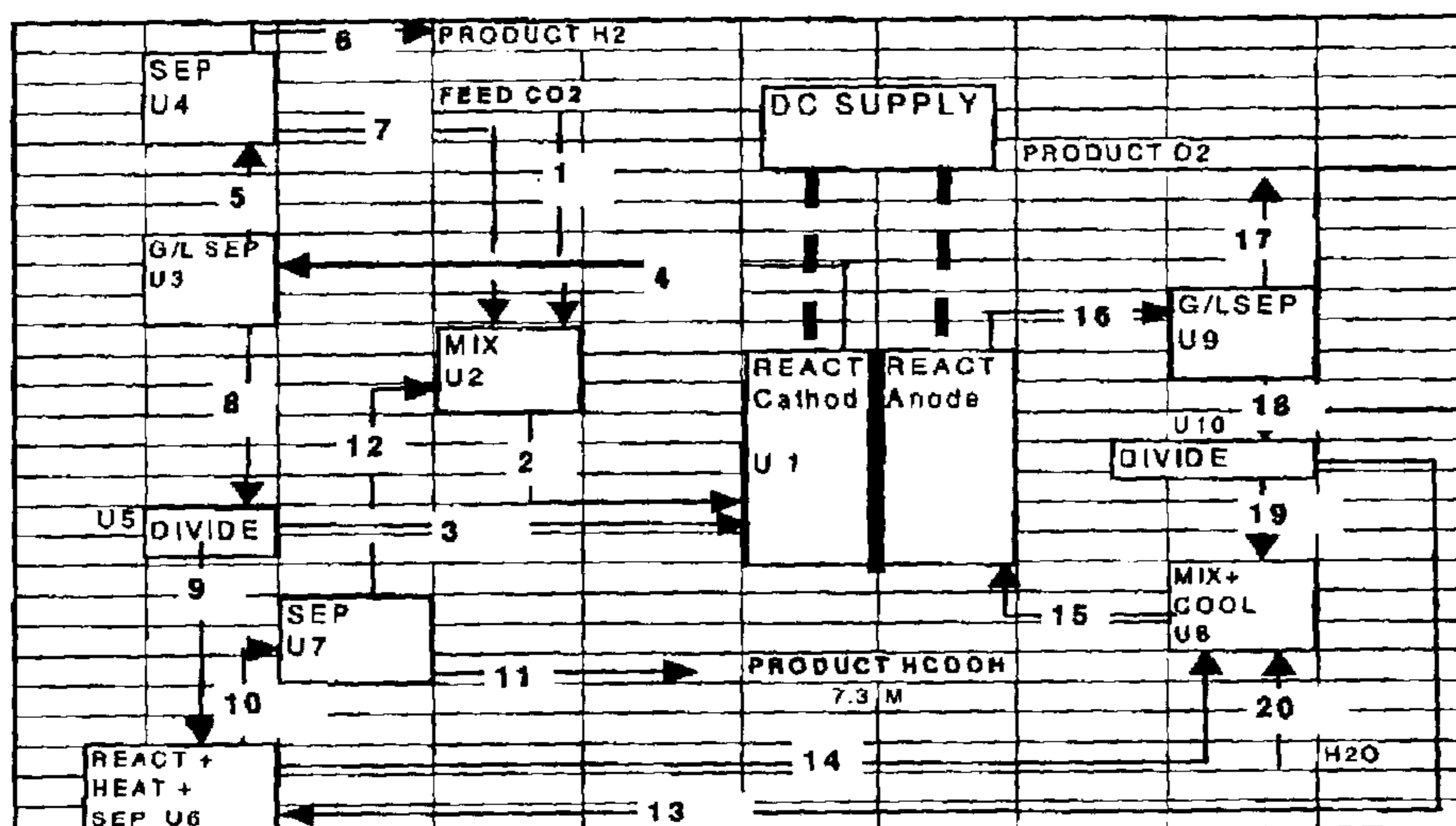
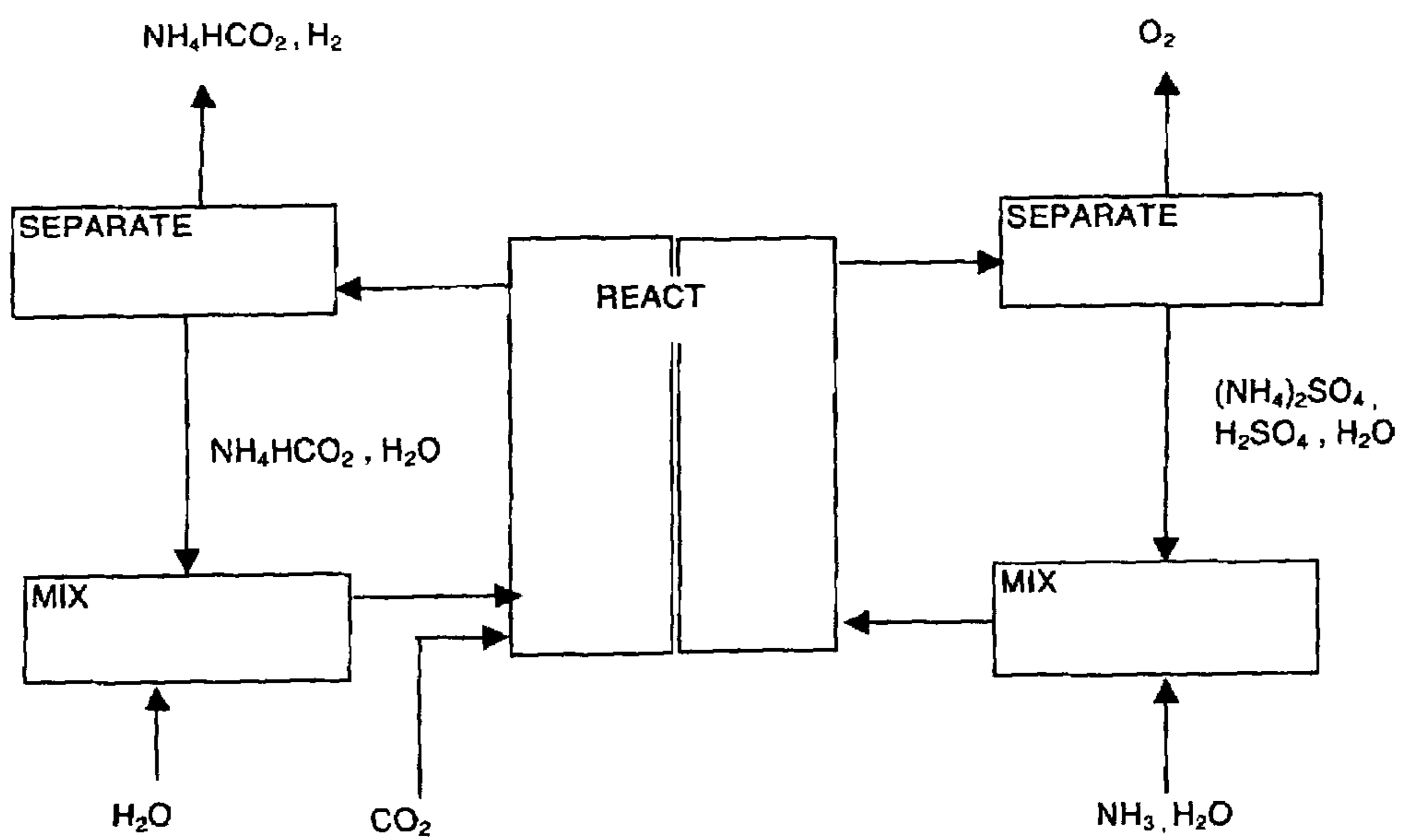


Figure 9



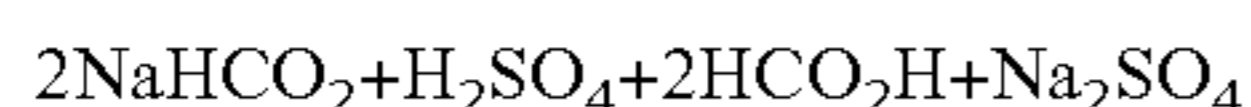
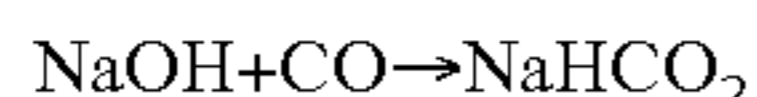
**CONTINUOUS CO-CURRENT  
ELECTROCHEMICAL REDUCTION OF  
CARBON DIOXIDE**

FIELD OF THE INVENTION

**[0001]** The invention is in the field of electrochemistry, encompassing processes for the electro-reduction of carbon dioxide in aqueous systems, and apparatus therefor.

BACKGROUND OF THE INVENTION

**[0002]** The formate salts  $M\text{HCO}_2$  (where M is typically Na, K or  $\text{NH}_4$ ) and formic acid  $\text{HCO}_2\text{H}$  are commercial chemicals that may be produced by industrial thermochemical processes (Kirk-Othmer—*Encyclopedia of Chemical Technology*, 1991). For example, sodium formate and subsequently formic acid may be obtained by reaction of sodium hydroxide with carbon monoxide, followed by acidolysis with sulphuric acid.



**[0003]** Formic acid may also be produced as a co-product in the oxidation of hydrocarbons and by the hydrolysis of methyl formate from the carbonylation of methanol. Processes for the synthesis of formate salts (e.g.  $\text{KHCO}_2$ ) by the electro-reduction of carbon dioxide are also known (Chaplin and Wragg, 2003; Sanchez et al., 2001; Akahori et al., 2004; Hui and Oloman, 2005).

**[0004]** Carbon dioxide is considered the main anthropogenic cause of climate change. Methods to sequester  $\text{CO}_2$  and/or convert it to useful products are therefore needed.

**[0005]** Oloman and Watkinson in U.S. Pat. Nos. 3,969,201 and 4,118,305 (incorporated herein by reference) describe a trickle bed reactor for electroreduction of oxygen to alkaline peroxide. In various aspects, that electrochemical cell comprises a pair of spaced apart electrodes, at least one of the electrodes being in the form of a fluid permeable conductive mass separated from the counter electrode by a barrier wall. The electrode mass may be in the form of a bed of particles or a fixed porous matrix. It is composed of an electronically conducting material the surface which is a good electrocatalyst for the reaction to be carried out. Inlets are provided for feeding liquid electrolyte and gas into the electrode mass such that the electrolyte and gas move co-currently through the electrode mass, for example in a direction generally perpendicular to the direction of the current between the electrodes. An outlet is provided for removing solutions containing reaction products from the fluid permeable conductive mass.

SUMMARY OF THE INVENTION

**[0006]** In various embodiments, the invention provides electro-chemical processes for reduction of carbon dioxide, for example converting carbon dioxide to formate salts or formic acid. In selected embodiments, operation of a continuous reactor with a three dimensional cathode and a two-phase (gas/liquid) catholyte flow provides advantageous conditions for electro-reduction of carbon dioxide. In these embodiments, the continuous two-phase flow of catholyte solvent and carbon dioxide gas, in selected gas/liquid phase volume ratios, provides dynamic conditions that favour the electro-reduction of  $\text{CO}_2$  at relatively high effective superficial current densities. In some embodiments, relatively high internal

gas hold-up in the cathode chamber (evident in a gas to liquid phase volume ratio  $>1$  in the feed stream, or  $>0.1$  within the porous electrode) may provide greater than equilibrium  $\text{CO}_2$  concentrations. In the liquid phase, facilitating relatively high effective superficial current densities. In some embodiments, these characteristics may for example be achieved at catholyte  $\text{pH} > 7$  and relatively low  $\text{CO}_2$  partial pressures ( $<10$  bar).

**[0007]** In alternative aspects, the invention involves continuously passing a catholyte mixture through a cathode chamber of an electrochemical reactor. The catholyte mixture may include carbon dioxide gas and a liquid catholyte solvent containing dissolved carbon dioxide. The catholyte solvent may for example be an aqueous solvent, it may include a dissolved alkali metal or ammonium bicarbonate, and may be maintained at a desired  $\text{pH}$ , such as in the range of from about 6 to about 9. A catholyte gas to liquid (G/L) volumetric ratio may be maintained, being the ratio of the volume of carbon dioxide gas to the volume of the liquid catholyte solvent. The G/L ratio may be maintained in the cathode chamber, for example in the feed stream or in a porous cathode within the chamber. For example, the process may be operated so that the G/L ratio is greater than a threshold value, such as greater than 1 in the feed, or greater than 0.1 within the porous (3D) cathode.

**[0008]** One aspect of the invention involves passing an electric current between a cathode in the cathode chamber and an anode, to reduce dissolved carbon dioxide to form a desired product. In some embodiments, the process may be operated so that the effective superficial current density at the cathode is greater than a threshold value, such as  $1 \text{ kA/m}^2$  (or  $1.5, 2, 2.5, 3, 3.5, 4, 4.5$  or  $5 \text{ kA/m}^2$ ). The electric current in the system may for example be a direct current, driven by an electrochemical cell voltage, and in some embodiments the process may be capable of operating at relatively low electrochemical cell voltages, for example less than 10 Volts.

**[0009]** Various aspects of the invention work in concert to facilitate the adoption, in some embodiments, of process parameters that may improve the economics of processes of the invention. In some embodiments, the processes of the invention may be used with relatively dilute input gas streams, for example the carbon dioxide gas concentration in the feed gas may be from 1 to 100%, or any numeric value within this range (in some embodiments yielding a carbon dioxide partial pressure in the cathode chamber less than a threshold value, such as 3, 5 or 10 Bar). Similarly, relatively low system pressures may be used, for example the cathode chamber may be maintained at a cathode pressure in the range of a minimum value such as 1, 2, 3, 4 or 5 Bar (1 Bar= $100 \text{ kPa(abs)}$ ) up to a higher maximum value such as 6, 7, 8, 9 or 10 Bar. In some embodiments, it may be effective to run processes of the invention at elevated temperatures, which may avoid the necessity for cooling, for example at cathode temperatures above a desired threshold such as 20, 25, 30, 35, 40, 45 or  $50^\circ \text{C}$ . In this context, it will be understood that cathode chamber pressures and temperatures may vary along the cathode height. For example, the inlet pressure may be greater than outlet pressure (in some embodiments, the pressure drop may for example range from a minimum of about 10, 20, 30, 40, or 50 kPa, up to a maximum of about 500, 600, 700, 800 or 900 kPa). Similarly, the outlet temperature may be greater than inlet temperature, with a temperature rise from the inlet to the outlet of from about 1 to  $100^\circ \text{C}$ ., or any numeric value within this range. It will be understood that the

gas composition (particularly CO<sub>2</sub> concentration) and the total pressure, fix the CO<sub>2</sub> partial pressure. i.e.  $ppCO_2 = (CO_2 \text{ fraction}) \times (\text{Total pressure})$

**[0010]** Cathodes for use in the invention may have an effective thickness in the dimension of current flow, such as a porous cathode. These may be referred to as three dimensional (3D) electrodes. Such electrodes may have a selected thickness, such as less than 6, 5, 4, 3, 2, 1 or 0.5mm, and they may have a selected porosity, or range of porosities, such as 5 to 95% or any numeric value within this range, such as 30, 40, 50, 60 or 70%. Cathodes of the invention may be made from a wide variety of selectively electro-active materials, such as tin, lead, pewter, mercury, indium, zinc, cadmium, or other materials such as electronically conductive or non-conductive substrates coated with selectively electro-active materials (e.g. tinned copper, mercury amalgamated copper, tinned graphite or tinned glass).

**[0011]** The anode may be in an anode chamber, and the anode chamber may be separated from the cathode chamber by an electrochemical cell membrane. The anolyte in the anode chamber may be an aqueous anolyte, and may for example include a dissolved alkali metal hydroxide, a salt (including an ammonium salt) or an acid, and may have a pH range of from about 0 to about 14, or any pH value or range within this range.

**[0012]** The electrochemical cell membrane may be a cation permeable membrane, for example a membrane that permits selected ions to cross the membrane to balance process stoichiometry.

**[0013]** The desired products of the process include formate salts, such as ammonium, potassium and sodium formate, or formic acid. The desired product may be separated from the catholyte solvent in a variety of ways. For example, a portion of the catholyte solvent, the recycling catholyte solvent, may be recycled from a cathode chamber outlet to a cathode chamber inlet, and the desired product may be separated from the recycling catholyte solvent. Similarly, at least a portion of the anolyte may be recycled from an anolyte chamber outlet to an anolyte chamber inlet, and an anode co-product may be separated from the recycling anolyte,

**[0014]** In selected embodiments, Joule heating of the anolyte may be used to provide heated anolyte, and the heated anolyte may be used to heat the recycling catholyte solvent to separate the desired product from the recycling catholyte solvent, for example by evaporation with fractional crystallization or vacuum distillation. In some embodiments, recycling catholyte, that includes formate, may be reacted with the anolyte, to obtain the desired product by an acidolysis reaction.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0015]** FIG. 1: is a process flow sheet illustrating aspects of the process of Example 1, in which A=ammeter, P=pressure gauge, T=thermometer, V=voltmeter, W=wet gas flow meter, PC=pressure control.

**[0016]** FIG. 2: is a schematic illustration of electrochemical cells of the invention, as described in Example 1, in which the reference numerals denote the following components: 1 and 2: cell bodies; 2, 7 and 9: gaskets; 3: anode feeder, 4: anode spacer; 5: membrane; 6: 3-D cathode (tin-coated copper mesh, tin shot/granules and Pb shot/granules); 8: cathode feeder.

**[0017]** FIG. 3 shows a sectioned elevation view of the single-cell reactor of the invention, Reactor A, as described in more detail in Example 1.

**[0018]** FIG. 4: shows a sectioned elevation view of the single-cell reactor of the invention, Reactor B, as described in more detail in Example 1.

**[0019]** FIG. 5: is a process flow sheet illustrating various aspects of a continuous process for conversion of CO<sub>2</sub> to formate salts or formic acid, involving recycling of catholyte and anolyte.

**[0020]** FIG. 6: Is a process flowsheet (Flowsheet "A"), illustrating an embodiment of the process for converting CO<sub>2</sub> gas to NaHCO<sub>2</sub> (sodium formate) and NaHCO<sub>3</sub> (sodium bicarbonate) with a byproduct of H<sub>2</sub> (hydrogen) and co-product of O<sub>2</sub> (oxygen).

**[0021]** FIG. 7: is a formalized version of process Flowsheet A, forming the basis for a steady-state material balance stream table for a process of converting approximately 600 tonnes per day of carbon dioxide gas to sodium formate.

**[0022]** FIG. 8: illustrates Process Flowsheet B, for which there is a corresponding material and energy balance stream table in the examples.

**[0023]** FIG. 9: illustrates Process Flowsheet C of the Examples.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0024]** In various aspects, the invention provides a continuous reactor for electroreduction of CO<sub>2</sub>, which may for example be used in a process that converts a feed of carbon dioxide plus water to formate ion (Reaction 1) and consequently produces formate salts or formic acid.



**[0025]** In some embodiments, the invention may utilize an electrochemical reactor analogous to the trickle bed reactor described by Oloman and Watkinson in U.S. Pat. Nos. 3,969,201 and 4,118,305. In such embodiments, the Invention may utilize an apparatus for carrying out electrochemical reactions involving gaseous reactants comprising an electrochemical cell having a pair of spaced apart electrodes, at least one of the electrodes, such as the cathode, being in the form of a fluid permeable conductive mass and being separated from the counter electrode by an ionically conductive but electronically insulating layer (such as a membrane or porous diaphragm). The reactor may be operated in a "trickle-bed" mode, with co-current flow of reactant gas and catholyte liquid through a flow-by 3-D cathode. As illustrated in the Examples, the process parameters of the invention may be adjusted so that this reactor achieves advantageous reactant supply (evident for example as a high gas space velocity, a ratio of the volumetric gas feed flow rate over reactor volume) and mass transfer characteristics. The co-current fluid flow in the cathode may be at any orientation relative to gravity, such as upward or downward.

**[0026]** In reactors of the invention, an inlet may be provided for feeding a liquid electrolyte and a gas into the fluid permeable conductive mass, and an outlet may be provided for removing solutions containing reaction products from the conductive mass. The inlet and outlet may be arranged so that the electrolyte and gas move co-currently through the conductive mass, for example in a direction generally normal to the flow of electric current between the electrodes. The reactor may for example be provided with a cation membrane

separator (as described for example in Hui and Oloman, 2005). In alternative embodiments, other types of reactor may be used.

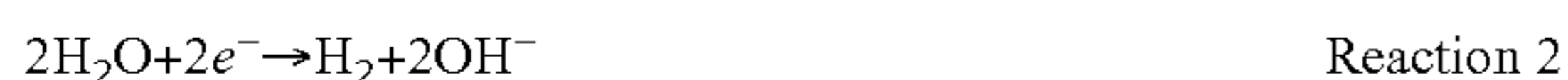
**[0027]** Depending on the desired products and overall material balance, the process feed may also include: metal hydroxides and/or metal salts such as MOH, MCl,  $M_2CO_3$ ,  $M_2SO_4$  and  $M_3PO_4$  where M is typically an alkali metal (Na, K, etc.) or  $NH_4$ ; acids such as  $H_2SO_4$ ,  $H_3PO_4$ , or HCl; or ammonia ( $NH_3$ ).

**[0028]** Flow sheets in various degrees of detail are provided for alternative processes in FIGS. 1, 5, 6, 7, 8 and 9, illustrating the range of embodiments encompassed by the invention. In selected embodiments, the feed  $CO_2$  stream to the process may be concentrated, for example to above 80% vol  $CO_2$ . Alternatively, a relatively dilute gas stream may be used, such as the product gas from combustion of a fossil fuel (typically containing about 10% vol  $CO_2$ ). Other potentially reactive components of the feed  $CO_2$  stream include oxygen, sulphur oxides, nitrogen oxides and hydrogen sulphide. These may be handled in the process in a variety of ways, for example they may be removed in one or more initial scrubbing steps, so that they are absent or at low concentrations (such as below about 1% vol) in the feed stream entering the reactor. The total pressure and temperature of the feed  $CO_2$  stream may vary over relatively wide ranges, for example from, respectively, about 100 to 1000 kPa(abs), and about 250 to 550 K. The conversion of  $CO_2$  per pass through the electrochemical reactor may be less than 100%, so that the invention may include provision for recycling the unconverted  $CO_2$  gas as well as recycling the catholyte liquid.

**[0029]** Process steps 1 to 5 in FIG. 5 may be included in some embodiments of the invention, briefly characterized as follows with reference to the annotations on the Figure.

**[0030]** Step 1. MIX: Continuously mixes the feed water (plus any make-up reagents) with the recycling catholyte, which is then delivered continuously to the reactor cathode chamber.

**[0031]** Step 2. REACT: [C] Cathode. Continuously drives reaction 1, along with the side-reaction, Reaction 2, that gives hydrogen by the electro-reduction of water.



**[0032]** Anode. Continuously drives the complimentary anode reaction(s) whose nature depends on the desired products from the process. For example, if the desired main product is a formate salt and the co-product is oxygen then the anode reaction may be Reaction 3.



**[0033]** If the desired main product is formic acid and the co-product is oxygen or chlorine then the anode reaction may be respectively Reaction 4 or 5. Other anode reactions may include the generation of peroxy-salts of peroxy-acids, such as peroxy-disulphate ( $2SO_4^- \rightarrow S_2O_8^{2-} + 2e^-$ ).



**[0034]** The electrode chambers in the reactor may be separated by a membrane that selectively allows the transport of cations from anode to cathode in amounts that balance the desired process stoichiometry. If the desired main product is a formate salt then these cations may be alkali metal ions (e.g.  $Na^+$ ,  $K^+$  or  $NH_4^+$ ) fed to the anolyte as hydroxides, salts or  $NH_3$  gas, whereas if the desired main product is formic acid

the transported cations may include protons ( $H^+$ ) generated in Reaction 4 and/or fed to the anolyte as an acid.

**[0035]** Step 3. SEPARATE: Continuously separates the main product (formate salt or formic acid) and byproduct (hydrogen) from the recycling catholyte.

**[0036]** Step 4. MIX: Continuously mixes required anode reagents and water with the recycling anolyte.

**[0037]** Step 5. SEPARATE: Continuously separates the anode co-product(s) from the recycling anolyte.

**[0038]** In various steps of the process, carbon dioxide and water may be consumed and/or generated. In other reactions, such as Reactions 6, 7 and 8 that occur in the reactor or elsewhere in the process.



**[0039]** In some embodiments, the process may involve driving the reactor at a relatively high superficial current density (e.g. above  $0.5 \text{ kA/m}^2$ ) and current efficiency, for example for formate production (e.g. above 50%). Processes of the invention may also involve balancing the material and energy requirements of the various process steps to match the required process stoichiometry, while maintaining a low specific energy consumption. For example, processes of the invention have demonstrated 75% current efficiency for formate at  $1.3 \text{ kA/m}^2$  with a reactor voltage of 3 V at  $CO_2$  pressure of 200 kPa(abs) and temperature of 300 K. The management of water may be important to the material balance and require that water be fed to the cathode and/or anode circuits to match its rate of reaction, electro-osmotic transport and evaporation. The consumption of energy in electrochemical reaction, heating, cooling and pumping may be a contributor to the process cost, and may be kept relatively low by appropriate reactor design and by rationalizing the thermal loads in the process. In some embodiments, non-metallic catalysts may be used. For example, U.S. Pat. Nos. 5,284,563 and 5,382,332 disclose nickel alkyl cyclam catalysts that may be used for carbon dioxide reduction.

**[0040]** In some embodiments, a relatively high gas/liquid (G/L) phase feed volumetric flow ratio may be used in the electrochemical reactor (e.g., G/L flow=1 to 1000 or 10 to 200), as well as a high gas space velocity (e.g.  $>100 \text{ h}^{-1}$ ). In selected reactors of the invention, increasing G/L from about 5 to 100 increases the voltage by less than 10%. The optimum G/L phase volume (denoted as the "G/L hold-up") ratio depends, in general, on the balance between the effective catholyte conductivity (usually decreasing with increasing G/L hold-up), the  $CO_2$  mass transfer capacity (usually increasing with increasing G/L hold-up) and the intrinsic temperature and pH dependent kinetics of  $CO_2$  conversion to the un-reactive bicarbonate/carbonate species in the bulk catholyte liquid phase.

**[0041]** In various embodiments, there are two separate gas/liquid (G/L) ratios that may be of importance:

**[0042]** (i) The volumetric G/L ratio in the reactor feed stream(s), with the gas volume flow corrected to STP, this may for example have a range of about 1 to 1000, 1 to 500, 10 to 200, or 10 to 100 or any numeric value within these ranges. For example, gas flow may be 1000 ml/min (corrected to STP), with liquid flow of 20 ml/min to give a G/L [flow] =  $1000/20=50$ .

**[0043]** (ii) The volumetric G/L ratio within the porous cathode, i.e. the ratio of gas hold-up to liquid hold-up in the cathode, which may for example have a range = about 0.1 to 10, or about 0.2 to 2, or 0.2 to 4, or any numeric value or range within these ranges. For example, gas hold up may be =0.6, with liquid hold-up =(1-0.6), to give G/L [hold-up] =0.6/0.4=1.5. Where, "Hold-up" = fraction of pore space (in 3D cathode) occupied by the specified phase at a given moment. Assumed to be constant in steady-state operation of the reactor. G/L[flow] is not equal to G/L[hold-up] because the gas has a shorter residence time in the cathode than the liquid (i.e. gas "slips" past the liquid). The feed stream and internal hold-up values of (i) and (ii) are of course related, since the value of (ii) depends on the value of (i) together with the cathode characteristics, such as porosity (or voidage), shape factor, and particle size. Similarly, the value of (i) affects the value of (ii), and is also related to the CO<sub>2</sub> mass transfer capacity in the cathode and the gas space velocity of the reactor.

**[0044]** The above conditions may be modulated to allow (where CD=current density):

**[0045]** Effective CD>1.5 kA/m<sup>2</sup> at CO<sub>2</sub> pressure<3 Bar.

**[0046]** Effective CD=[superficial CD]×[current efficiency for desired product (e.g. formate)]

**[0047]** Format product concentration >0.5 M in a single pass.

**[0048]** Total reactor voltage at 3 kA/m<sup>2</sup><Volt

**[0049]** The "superficial current density" is the current passing through the cell divided by the projected surface area of the relevant element, such as the cathode. The "projected surface area" of an element, such as the cathode, is surface area of a projection of the element on a plane parallel to the element. For flat plate elements, the projected surface area is equal to the area of the side of that element facing the other conductive element, for example the projected surface area of the cathode facing the anode. For an element in the form of a planar mesh, the projected surface area is the area within the outline of the mesh as projected onto a continuous planar surface.

**[0050]** The "current efficiency" (CE) is the ratio, generally expressed as a percentage, of the actual reaction rate to the rate that would be achieved if all of the current passing through the cell were consumed by relevant reaction, such as the reduction of carbon dioxide.

**[0051]** In some embodiments, the invention may operate at or near adiabatic conditions (T out, up to about 90° C.). In some embodiments, while reducing the solubility of CO<sub>2</sub> in the catholyte, an increasing temperature actually favours the intrinsic kinetics of the electroreduction of carbon dioxide (ERC), and good CE can be obtained at higher temperatures by manipulating the factors that promote CO<sub>2</sub> mass transfer in a continuous reactor. In some embodiments, the ability to operate at high temperature may be important, because the effects of Joule heating at high CD under near adiabatic conditions in the continuous reactor may automatically increase the reaction temperature by up to about 80° C.

#### EXAMPLE 1

**[0052]** FIG. 1 shows a process flow diagram reflecting this example of the electro-reduction of carbon dioxide (ERC). Pure CO<sub>2</sub> or the mixture of CO<sub>2</sub> (gas) and N<sub>2</sub> (gas) was combined with the catholyte (liquid) at a T junction (mixer), from which the gas and liquid proceeded in slug flow to enter the cathode chamber from the bottom. Thus, the electrochemical reactor was operated with co-current upward multiphase (G/L) flow on the cathode side. The anolyte, which was

an aqueous KOH solution, also flowed upward through the anode chamber and was recycled to the anolyte storage tank. All gases and liquids passed through individual rotameters. Liquid flow was controlled at the pumps, while gas flows were controlled by manual valves to assure the appropriate gas and liquid loads in the reactor. The reactor inlet and outlet pressures and temperatures were measured by visual gauges at the points indicated in the flowsheet. In runs during which the catholyte product temperatures were controlled, pre-cooling or pre-heating of both anolyte and catholyte was employed to keep the temperature at a desired level. Liquid product was withdrawn from the sampling point and analyzed for formate concentration. Gas product from the gas/liquid separator (a packed bed of graphite felt) was controlled by a 3-way valve either to an Orsat gas analyzer for CO<sub>2</sub> and CO analysis, to a wet gas flow meter for flow rate measurement, or to a Tedlar sampling bag for subsequent hydrocarbon analysis with gas chromatograph.

**[0053]** Galvanostatic electrolysis of CO<sub>2</sub> was carried out with a DC power supply connecting across the anode and cathode. A voltmeter was also connected to the unit to measure the reactor voltage. All voltages included anode potential, cathode potential and IR drop. The individual electrode potentials were not measured.

**[0054]** An automatic pressure control valve was used in the anolyte product line to balance the pressure in the anode chamber against that in the cathode chamber. Such a pressure balance is required to prevent catholyte by-passing the 3-D cathode and/or the bursting of the membrane that can occur when the cathode pressure exceeds the anode pressure.

**[0055]** Most runs were conducted with the cathode outlet at the atmospheric pressure. For some runs in Reactor B a manual back pressure control valve and pressure gauge were installed in the catholyte product line to maintain superatmospheric pressure in the catholyte outlet.

**[0056]** Processes of the invention were performed first in Reactor A (small reactor) and then in a seven-fold big Reactor B (big reactor) to evidence the effects of scale up. Both reactors have the configuration shown in FIG. 2. The reactors consist of a cathode feeder plate and a 3-D cathode, a Nafion cation exchange membrane separator, anode spacer/membrane support, an anode feeder plate and gaskets. The cathode mesh, anode mesh and the anode spacer are sealed on their margins by silicone glue, and then the cell assembly is sandwiched between insulated mild steel plates and uniformly compressed with SS bolts to give a balanced fluid distribution.

**[0057]** FIG. 3 shows a sectioned elevation view of the single-cell Reactor A. The "flow-by" cathode of this reactor had dimensions of 30 mm width and 150 mm height (geometric surface). The thickness of the cathode depended on which 3-D cathode material was used. For tin-coated copper mesh cathode, single or multiple layers of mesh were placed between the membrane and cathode feeder so the thickness of the cathode was the total thickness of these all layers, which ranged from 0.38 to 1.83 mm; for graphite felts and metal granules or shot, the cathode materials were embedded in two layers of Neoprene gasket with the back of the cathode in contact with the cathode feeder, therefore the thickness of the cathode was that of the gasket, i.e. 3.2 mm. The geometric (a.k.a. superficial) cathode area perpendicular to the electric current was 30 mm by 150 mm-4.5×10<sup>-3</sup> m<sup>2</sup>. In Reactor A the applied current ranged from 1 to 14 A with corresponding superficial current density from 0.22 to 3.11 kA m<sup>-2</sup>.

**[0058]** In Reactor B, tin-coated copper mesh cathodes or tin granule cathodes were used. FIG. 4 presents the dimensioned front view and corresponding dimensions of Reactor B with a tin granule fixed-bed cathode. To minimize the by-pass of the catholyte at the edges of the cathode bed, the gasket was purposely made with five triangles on each side to direct the flow toward the centre of the cathode. Subtracting the areas taken by those triangles, the superficial cathode area was  $3.22 \times 10^{-2} \text{ m}^2$ , which was about seven times that of Reactor A ( $4.5 \times 10^{-3} \text{ m}^2$ ). The applied current in Reactor B ranged from 20 to 101 A with corresponding superficial current density 0.62 to  $3.20 \text{ kA m}^{-2}$ .

**[0059]** Reactor B was assembled with a tin granule fixed-bed cathode, according to the following procedures: (1) A sanded tin plate (99.99 wt % Sn, 3mm thick) cathode feeder was put onto the neoprene gasket; (2) The pretreated tin granules were spread uniformly into a Durabla gasket (3.2 mm thick) on the tin plate, and layers of Netlon screen were inserted into the entrance and exit regions of the catholyte flow to distribute the fluid and support the membrane; (3) The wet Nafion 117 membrane was put on top of the tin granule bed, and then, the PVC screen spacer, anode SS mesh, and anode feeder (SS plate) were placed on top of one another in that sequence; (4) Lastly, a cell body was put into place, and 24  $\frac{3}{8}$  inch bolts were employed to compress the sandwiched cell uniformly.

**[0060]** A variety of cathode materials are available for use in alternative aspects of the invention. Carbon dioxide can be electrochemically reduced on almost all groups of metals in the periodic table to give a variety of products with different levels of selectivity. The following cathode materials, among others, may be adapted to particular embodiments: Nanostuctured Cu deposited on graphite felt; Cu/Sn alloy deposited on graphite felt; nano-structured Sn on Sn mesh, Sn coated plastic mesh, Cu mesh; Sn deposited graphite felt; Sn coated copper mesh; Pb plate, shot, granules, grid and Pb-C reticulate; Sn shot and granules. The last five of the foregoing materials were used in alternative embodiments for the present Example. In some embodiments, a high (specific) surface area micro or nano-structured deposit on a 3D substrate is desirable. Other potential cathodes are nano-structured Cu on Cu mesh, nano-structured Sn on Sn mesh, or Sn coated plastic mesh, alternatively with Pb, In or Hg as the electroactive surface.

**[0061]** Reactor A, using granulated tin cathodes (99.9 wt % Sn) and a feed gas of 100%  $\text{CO}_2$  showed slightly better performance than that of the tinned-copper mesh cathodes. The seven fold scaled-up Reactor B used a feed gas of 100%  $\text{CO}_2$  with the aqueous catholyte and anolyte respectively [0.5 M  $\text{KHCO}_3 + 2 \text{ M KCl}$ ] and 2 M KOH, at inlet pressure from 350 to 600 kPa(abs) and outlet temperature 295 to 325 K. For a superficial current density of 0.6 to  $3.1 \text{ kA m}^{-2}$  Reactor B achieved corresponding formate current efficiencies of 91 to 63%, with the same range of reactor voltage as that in Reactor A (2.7 to 4.3 V). Up to 1 M formate was obtained in the catholyte product from a single pass in Reactor B.

#### EXAMPLE 2

##### Recovery Of Cathode Activity

**[0062]** An electrochemical reactor as described in Example 1 was constructed and operated as follows:

**[0063]** Anode feeder=316 stainless steel plate

**[0064]** Anode=304 stainless steel number 10 mesh (10 mesh/inch)

**[0065]** Anode spacer=PVC "fly screen" 10 mesh.

**[0066]** Separator=Nafion 117 cation membrane.

**[0067]** Cathode=ca. 50 mesh tin granules. 150 mm high by 32 mm wide by 3 mm thick

**[0068]** Cathode superficial area= $45 \text{ E}4 \text{ m}^2$

**[0069]** Cathode feeder=tin foil supported on a copper plate

**[0070]** Operating conditions:

**[0071]** current=6 A (i.e.  $1.3 \text{ kA/m}^2$ ),

**[0072]** catholyte=0.45 M  $\text{KHCO}_3 + 2 \text{ M KCl}$ , anolyte=1 M KOH, anolyte flow=40 ml/min

**[0073]**  $\text{CO}_2$  gas flow=364 ml (STP)/min, catholyte flow=20 ml/min,

**[0074]** temperature=300 K, pressure=140-170 kPa(abs).

**[0075]** With a cathode of fresh tin granules the formate current efficiency (CE) dropped from about 60% at 30 minutes to 50% at 250 minutes operating time. Recovery of the current efficiency was achieved by:

**[0076]** (i). Chemical treatment and recycle of the cathode: The used cathode tin granules were treated in 11 wt % nitric acid at room temperature for 2 minutes, washed in deionized water and re-used in the reactor. Table 1 shows that this treatment regained the cathode activity at 30 minutes operating time.

TABLE 1

No. of recycles	Formate CE at 30 min %	Reactor voltage V	Cathode feed pressure kPa(abs)
0 (fresh granules)	63	3.73	156
1	61	3.56	156
2	64	3.36	161
3	66	3.30	166

**[0077]** Similar results for cathode recovery were obtained by treating the used tin granules with hydrochloric acid and/or potassium hydroxide.

**[0078]** (ii). Polarity reversal: Under similar conditions to those above, with fresh tin granules the formate current efficiency dropped from 65% at 30 minutes to 48% at 360 minutes operating time. Polarity reversal was applied to the reactor for 5 minutes at 1 A. The formate current efficiency subsequently increased and was back to 65% at 400 minutes operating time.

#### EXAMPLE 3

##### Scale-Up

**[0079]** An electrochemical reactor as described in Example 1 was constructed and operated as follows:

**[0080]** Anode feeder=316 stainless steel plate

**[0081]** Anode=304 stainless steel, number 10 mesh (10 mesh/inch)

**[0082]** Anode spacer=PVC "fly screen", 10 mesh.

**[0083]** Separator=Nafion 117 cation membrane.

**[0084]** Cathode=ca. 50 mesh tin granules. 680 mm high by 50 mm wide by 3 mm thick

**[0085]** Cathode superficial area= $340 \text{ E}4 \text{ m}^2$

**[0086]** Cathode feeder=2 mm thick tin plate.

**[0087]** Operating conditions:

**[0088]** catholyte=0.45 M  $\text{KHCO}_3 + 2 \text{ M KCl}$ , anolyte=2 M KOH, anolyte flow=60 ml/min

[0089] CO<sub>2</sub> gas flow=1600-2200 ml (STP)/min, catholyte flow=20 ml/min,

[0090] temperature in-out=300-314 K, pressure In-out=600-100 kPa(abs).

[0091] Table 2 shows the performance of this reactor.

TABLE 2

Reactor performance.				
Current, A	20	40	94	100
Superficial current density, kA/m <sup>2</sup>	0.6	1.2	2.9	3.1
Operating time, min	60	80	100	17
Formate CE, %	91	86	64	63
Formate product conc, M	0.28	0.54	0.94	1.03
Reactor voltage, V	2.7	3.4	4.1	3.9

## EXAMPLE 4

## Acid Anolyte

[0092] A reactor was constructed as in Example 1, operation was as in Example 2, except the anolyte was replaced by an acid sodium sulphate solution as follows:

[0093] Operating conditions:

[0094] catholyte=0.45 M KHCO<sub>3</sub>+2 M KCl,

[0095] anolyte=0.5 to 2 M Na<sub>2</sub>SO<sub>4</sub>+0.5 to 4 M H<sub>2</sub>SO<sub>4</sub>, anolyte flow=40 ml/min

[0096] CO<sub>2</sub> gas flow=500 ml (STP)/min, catholyte flow=20 ml/min,

[0097] temperature=300 K, pressure=140-170 kPa(abs).

[0098] The reactor was operated over a current range from 1 to 14 A (0.2 to 3.1 kA/m<sup>2</sup>) with corresponding formate CE from 80 to 30% and reactor voltage from 3.5 to 8.0 V.

[0099] This result shows that the process can be operated with an acid anolyte. The various ratios of Na<sup>+</sup>/H<sup>+</sup> in the anolyte gave different formate current efficiencies, thus indicating that the formate CE could be improved by manipulating the anolyte composition.

## EXAMPLE 5

## Ammonium Cations

[0100] In some embodiments, the invention may utilize ammonium cations, to produce ammonium formate. A reactor was constructed as in Example 1, operation was as in Example 4, except the catholyte potassium cations were replaced by ammonium and the anolyte was replaced by an acid ammonium sulphate solution, as follows:

[0101] Operating conditions:

[0102] current=4 A (i.e. 0.89 kA/m<sup>2</sup>)

[0103] catholyte=0.45 M NH<sub>4</sub>HCO<sub>3</sub> +2 M NH<sub>4</sub>Cl,

[0104] anolyte=0.93 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>+0.75 4 M H<sub>2</sub>SO<sub>4</sub>, anolyte flow=40 ml/min

[0105] CO<sub>2</sub> gas flow=500 ml (STP)/min, catholyte flow=20 ml/min,

[0106] temperature=300 K, pressure=140-170 kPa(abs).

[0107] The reactor was operated over 2 hours with formate CE ranging from 35 to 70% and reactor voltage from 4.6 to 5.2 V.

[0108] This result demonstrates that the process can use exclusively ammonium cations in the catholyte. The ability to

use ammonium cations is illustrated in Process Flowsheets B and C, for the production of formic acid/or ammonium formate.

## EXAMPLE 6

## Lead Cathode

[0109] An electrochemical reactor as described in Example 1 was constructed and operated as follows:

[0110] Anode feeder=316 stainless steel plate

[0111] Anode=304 stainless steel number 10 mesh (10 mesh/inch)

[0112] Anode spacer=PVC "fly screen" 10 mesh.

[0113] Separator=Nafion 117 cation membrane.

[0114] Cathode=0.5 mm diameter lead shot. 150 mm high by 32 mm wide by 3 mm thick.

[0115] Cathode superficial area=45E-4 m<sup>2</sup>

[0116] Cathode feeder=lead plate.

[0117] Operating conditions:

[0118] current=6 A (i.e. 1.3 kA/m<sup>2</sup>),

[0119] catholyte=0.45 M KHCO<sub>3</sub>+2 M KCl, anolyte=1 M KOH, anolyte flow=40 ml/min

[0120] CO<sub>2</sub> gas flow=364 ml (STP)/min, catholyte flow=20 ml/min,

[0121] temperature=300 K, pressure=140-180 kPa(abs).

[0122] Operation of this reactor over a period from 2 to 6 hours showed a constant formate current efficiency of 31+/-1%.

## EXAMPLE 7

## Process Flowsheet A

[0123] The process of this Example is illustrated in FIG. 6, showing electro-synthesis of sodium formate from carbon dioxide, water and sodium hydroxide.

[0124] Based on the concept of FIG. 5 this process (FIG. 6) converts CO<sub>2</sub> to NaHCO<sub>2</sub> (sodium formate) and NaHCO<sub>3</sub> (sodium bicarbonate) with a byproduct of H<sub>2</sub> (hydrogen) and co-product of O<sub>2</sub> (oxygen). The feed plus recycle CO<sub>2</sub> is compressed to about 300 kPa(abs) and delivered to the cathode of the electrochemical reactor along with the recycling catholyte, an aqueous solution of NaHCO<sub>2</sub> and NaHCO<sub>3</sub>. The cathode outlet goes to a gas/liquid separator from which the liquid is divided into a direct recycle and a stream from which NaHCO<sub>2</sub> and NaHCO<sub>3</sub> are separated by evaporation and fractional crystallization to give the main cathode products (NaHCO<sub>2</sub> and NaHCO<sub>3</sub>). The cathode outlet gas goes to a gas separation system (e.g. pressure swing adsorption) that recovers H<sub>2</sub> and delivers the unconverted CO<sub>2</sub> to recycle. The anode side of this process involves a feed of NaOH (sodium hydroxide) whose sodium content (Na<sup>+</sup>) is transported across the cation membrane while the hydroxide is converted to oxygen that is recovered as the co-product from a gas/liquid separator. The recycle streams in this process include the necessary compressors and pumps along with heat exchangers (e.g. C1, C2, C3) to control the reactor temperature in the range of about 300 to 350 K.

[0125] FIG. 7 illustrates Process Flowsheet A, and the steady-state material balance stream table is set out below, based on 600 tonne/day CO<sub>2</sub>. Formate current efficiency=77%. CO<sub>2</sub> conversion/pass=72%.



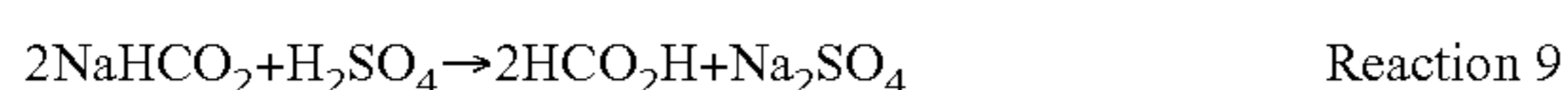
Basis: 600 Ton/day CO <sub>2</sub>											
Stream table				Flow rate of components in kmol/h							
Stream	phase	Tempt.	Volume	Density	CO <sub>2</sub>	NaHCO <sub>3</sub>	HCOONa	H <sub>2</sub>	O <sub>2</sub>	NaOH	H <sub>2</sub> O
			m <sup>3</sup> /h	kg/m <sup>3</sup>							
1	G	293	13868		567	0	0	0	0	0	0
2	G	293	19298		789	0	0	0	0	0	0
3	L	288	319	1150	0	0	0	0	0	638	18975
4	G/L	321			222	508	1814	65	0	0	
5	G/L	321			0	0	0	0	142	71	
6	L	321	319	1150	0	0	0	0	0	71	20235
7	S	298	23		0	0	0	0	0	567	0
8	G	321	3467		0	0	0	0	142	0	0
9	G	321	7024		222	0	0	65	0	0	0
10	L	321	319	1150	0	508	1814	0	0	0	11166
11	G	321	1595		0	0	0	65	0	0	0
12	G	321	5430		222	0	0	0	0	0	0
13	L	321	301	1150	0	479	1711	0	0	0	10528
14	L	321	18	1150	0	29	104	0	0	0	638
15	L	379	178	1150	0	0	0	0	0	0	549
16	L/S	379			L/S	L/S	L/S	L/S	L/S	L/S	554
17	L	298	123	1350	0	151	1719	0	0	0	2038
18	S	298	27		0	329	0	0	0	0	0
19	L	288	194	1000	0	0	0	0	0	0	600
21	L	298	107	1350	0	131	1490	0	0	0	31780
20	L	288	319	1150	0	160	1596	0	0	0	14359
22	L	298	16	1350	0	20	229	0	0	0	272

## EXAMPLE 8

## Process Flowsheet B

**[0126]** FIG. 8 illustrates the electrosynthesis of formic acid from carbon dioxide and water. The exemplified process converts CO<sub>2</sub> to HCO<sub>2</sub>H (formic acid) with a byproduct of H<sub>2</sub> (hydrogen) and co-product of O<sub>2</sub> (oxygen). The feed plus recycle CO<sub>2</sub> is compressed to about 300 kPa(abs) and delivered to the cathode of the electrochemical reactor (U1) along with the recycling catholyte, an aqueous solution of NH<sub>4</sub>HCO<sub>2</sub> and NH<sub>4</sub>HCO<sub>3</sub> plus (if required) a supporting electrolyte such as NH<sub>4</sub>Cl or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. The cathode outlet stream goes to a gas/liquid separator (U3) from which the liquid is divided (U5) into a direct recycle and a stream that is passed to a thermochemical acidolysis reactor/separator (U6, U7) where formic acid is obtained by reaction 9 with sulphuric acid (generated in the anolyte) and distilled under partial vacuum to give an overhead product of aqueous formic acid and a bottoms solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> that is recycled to the anode via the mixer U8. The gas stream from U3 passes to a separator (U4) where H<sub>2</sub> is recovered and CO<sub>2</sub> is recycled to the reactor feed via mixer U2, along with CO<sub>2</sub> generated by the side-reaction 7 in the acidolysis reactor.

**[0127]** An aqueous solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> recycles through the anode circuit, supplying NH<sub>4</sub><sup>+</sup> and H<sup>+</sup> cations for transport to the catholyte via the cation membrane. The co-product O<sub>2</sub> gas is generated with protons (H<sup>+</sup>) at the anode by reaction 4 and recovered from a gas/liquid separator (U9). The recycling acid anolyte is then divided (U10) to supply H<sub>2</sub>SO<sub>4</sub> for the acidolysis reaction (U6) from which the spent reactant is re-combined with the anolyte (U8).



**[0128]** A material and energy (M&E) balance for Flowsheet B operating at steady-state is shown in the stream table below. This M&E balance is based on the assumption of a formate current efficiency of 80% and 80% conversion of CO<sub>2</sub> per pass through the electrochemical reactor.

**[0129]** The primary and secondary net reactions in Flowsheet B are respectively reactions 10 and 11.



**[0130]** The conditions of this process may be chosen to promote the main net reaction 10. The characteristics of the process of this example, to promote reaction 10 may be selected as follows:

**[0131]** i. Appropriate electrode materials, current density, fluid compositions, fluid loads, pressure and temperature in the electrochemical reactor.

**[0132]** ii. Maintaining the anolyte composition with respect to acid and salt to provide cation transport across the membrane in the correct ratio (e.g. H<sup>+</sup>/NH<sub>4</sub><sup>+</sup>) that balances the rates of cathode reactions 1 and 2 and holds the catholyte pH in the desired range.

**[0133]** iii. A bulk catholyte pH in the range about 4 to 10, preferably 6 to 8.

**[0134]** iv. Maintaining the anolyte composition and flow to provide protons for the acidolysis reaction that produces HCO<sub>2</sub>H in U6 and allow recovery of the aqueous formic acid by vaporization in U7.

**[0135]** v. A concentration of acid (e.g. H<sub>2</sub>SO<sub>4</sub>) in the anolyte of greater than about 1 M.

**[0136]** vi. Maintaining the formate concentration of the catholyte sufficiently high to allow formation and separation of HCO<sub>2</sub>H in U6.

**[0137]** vii. A concentration of formate (HCO<sub>2</sub><sup>-</sup>) in the recycle catholyte of greater than about 1 M, preferably about 5 M.

**[0138]** viii. Feeding water to the cathode and/or anode circuits at the appropriate rate(s) to maintain the water balance and the electrolyte concentrations that facilitate both the electrochemical and thermochemical processes in U1, U6 and U7.

[0139] ix. Maintaining the flow and temperature of the recycle anolyte sufficiently high to utilize the Joule heating of the electrochemical reactor for evaporation of formic acid in U6.

[0140] x. A recycle anolyte temperature of greater than about 320 K, with an anolyte flow determined by the energy balance to reduce the need for heating utilities in the process.

[0141] Operation of the process will typically depend on interactions among the conditions i to x listed above. Modeling of this embodiment provided a steady-state material and energy balance, on the basis of 105 tonne/day CO<sub>2</sub>, giving a current efficiency of 80% and CO<sub>2</sub> conversion/pass of 80%. The material and energy balance stream table corresponding to Process flowsheet B is set out below, with the Table continued across the three sub-tables.

Stream table									
Comp.	M kg/kmol	Stream 1	2	kmol/h		BASIS 5	105 6	Ton/day 7	CO2 8
CO2	44	100.0	139.2	0.0	27.8	27.8	0.0	27.8	0.0
H2	2	0.0	0.0	0.0	25.0	25.0	25.0	0.0	0.0
N2	28	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H2O	18	314	332	5873	6693	17	0	17	6676
HCOOH	46	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NH4HCO2	63	0.0	0.0	731.4	831.4	0.0	0.0	0.0	831.4
NH4HCO3	79	0.0	0.0	83.1	94.5	0.0	0.0	0.0	94.5
(NH4)2SO4	132	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H2SO4	98	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
O2	32	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	kg/h	1.0E+04	1.2E+04	1.6E+05	1.8E+05	1.6E+03	5.0E+01	1.5E+03	1.8E+05
Phase		G + L	G + L	L	G + L	G	G	G	L
Pressure	kPa(abs)	100	300	300	200	200	800	100	100
Temp	K	300	300	300	354	354	300	300	354
Density	kg/m3			1083					1083
Volume	m3/h	2494	1157	146		1035	78	1128	166
Enthalpy	kJ/h	-1.2E+08	-1.4E+08	-2.5E+09	-2.8E+09	-1.5E+07	1.5E+03	-1.5E+07	-2.8E+09

Stream table							
Comp.	M	9	10	11	12	13	14
CO2	44	0.0	11.4	0.0	11.4	0.0	0.0
H2	2	0.0	0.0	0.0	0.0	0.0	0.0
N2	28	0.0	0.0	0.0	0.0	0.0	0.0
H2O	18	803	550	550	0	1101	1365
HCOOH	46	0.0	100.0	100.0	0.0	0.0	0.0
NH4HCO2	63	100.0	0.0	0.0	0.0	0.0	0.0
NH4HCO3	79	11.4	0.0	0.0	0.0	0.0	0.0
(NH4)2SO4	132	0.0	0.0	0.0	0.0	181.7	237.4
H2SO4	98	0.0	0.0	0.0	0.0	55.7	0.0
O2	32	0.0	0.0	0.0	0.0	0.0	0.0
Total	kg/h	2.2E+04	1.5E+04	1.4E+04	5.1E+02	4.9E+04	5.6E+04
Phase		L	G	L	G	L	L
Pressure	kPa(abs)	100	10.0	100	100	100	100
Temp	K	354	319	300	300	354	319
Density	kg/m3	1083		1061		1356	1322
Volume	m3/h	20	175437	14	294	36	42
Enthalpy	kJ/h	-3.4E+08	-1.7E+08	-2.0E+08	-4.6E+06	-5.8E+08	-6.8E+08

Stream table							
Comp.	M	15	16	17	18	19	20
CO2	44	0.0	0.0	0.0	0.0	0.0	0.0
H2	2	0.0	0.0	0.0	0.0	0.0	0.0
N2	28	0.0	0.0	0.0	0.0	0.0	0.0
H2O	18	18415	17790	61	17729	16628	422
HCOOH	46	0.0	0.0	0.0	0.0	0.0	0.0
NH4HCO2	63	0.0	0.0	0.0	0.0	0.0	0.0
NH4HCO3	79	0.0	0.0	0.0	0.0	0.0	0.0
(NH4)2SO4	132	2981	2925.6	0.0	2925.6	2743.9	0.0
H2SO4	98	841	896.6	0.0	896.6	840.9	0.0
O2	32	0.0	62.5	62.5	0.0	0.0	0.0
Total	kg/h	8.1E+05	8.0E+05	3.1E+03	7.9E+05	7.4E+05	7.6E+03

-continued

Phase		L	G + L	G	L	L	L
Pressure	kPa(abs)	300	200	100	100	100	100
Temp	K	300	354	354	354	329	300
Density	kg/m <sup>3</sup>	1349			1356	1356	1000
Volume	m <sup>3</sup> /h	585		1804	585	549	8
Enthalpy	kJ/h	-9.7E+09	-9.4E+09	-1.5E+07	-9.4E+09	-8.8E+09	-1.2E+08

## EXAMPLE 9

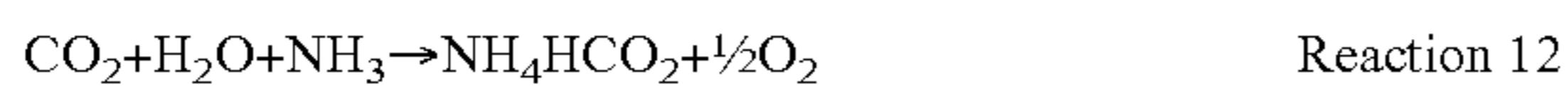
## Process Flowsheet C

[0142] FIG. 9 illustrates electro-synthesis of ammonium formate from carbon dioxide, ammonia and water. This process converts CO<sub>2</sub> and NH<sub>3</sub> to NH<sub>4</sub>HCO<sub>2</sub> (ammonium formate) with a byproduct of H<sub>2</sub> (hydrogen) and co-product of O<sub>2</sub> (oxygen).

[0143] The feed plus recycle CO<sub>2</sub> is compressed and delivered to the cathode of the electrochemical reactor along with the recycling catholyte, an aqueous solution of NH<sub>4</sub>HCO<sub>2</sub> (e.g. >1 M) with minor amounts of NH<sub>4</sub>HCO<sub>2</sub> (ammonium bicarbonate—e.g. 0.1 M). The cathode outlet stream goes to separation system that recovers a solution of NH<sub>4</sub>HCO<sub>2</sub> plus the byproduct hydrogen and recycles the spent catholyte.

[0144] Ammonia (NH<sub>3</sub> gas or aqueous solution) is fed to the anolyte circuit where it combines to form (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (ammonium sulphate). An aqueous solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> then recycles through the anode circuit, supplying NH<sub>4</sub><sup>+</sup> and H<sup>+</sup> cations for transport to the catholyte via the cation membrane. The co-product O<sub>2</sub> gas is generated with protons (H<sup>+</sup>) at the anode by reaction 4 and recovered from a gas/liquid separator. The ratio [NH<sub>4</sub><sup>+</sup>]/[H<sup>+</sup>] is maintained in the anolyte to supply these species to the catholyte at rates that balance the stoichiometry of reactions 1 and 2 and produce a catholyte solution of predominantly ammonium formate at pH in the range about 4 to 8.

[0145] The primary and secondary net reactions in flow-sheet C are respectively reactions 12 and 13.



[0146] Variations of this scheme may include for example replacement of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> in the anolyte by (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> or by NH<sub>4</sub>Cl and HCl. In the later case the anode co-product may be Cl<sub>2</sub> by reaction 5. Anode co-products may also include peroxy-compounds such as ammonium persulphate (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> or persulphuric acid H<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, etc. by reaction 14.



## REFERENCES

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[0155] Although various embodiments of the invention are disclosed herein, many adaptations and modifications may be made within the scope of the Invention in accordance with the common general knowledge of those skilled in this art. Such modifications include the substitution of known equivalents for any aspect of the invention in order to achieve the same result in substantially the same way. Numeric ranges are inclusive of the numbers defining the range. The word “comprising” is used herein as an open-ended term, substantially equivalent to the phrase “including, but not limited to”, and the word “comprises” has a corresponding meaning. As used herein, the singular forms “a”, “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a thing” includes more than one such thing. Citation of references herein is not an admission that such references are prior art to the present invention. Any priority document(s) and all publications, including but not limited to patents and patent applications, cited in this specification are incorporated herein by reference as if each individual publication were specifically and individually indicated to be incorporated by reference herein and as though fully set forth herein. The invention includes all embodiments and variations substantially as hereinbefore described and with reference to the examples and drawings.

1. An electrochemical process for reducing carbon dioxide comprising:

- continuously passing a catholyte mixture through a cathode chamber of an electrochemical reactor, the catholyte mixture comprising carbon dioxide gas and a liquid catholyte solvent containing dissolved carbon dioxide;
- maintaining a catholyte gas to liquid volumetric hold-up ratio, being the ratio of the volume of gas to the volume of the liquid catholyte solvent, in the cathode chamber, greater than about 0.1.

- c) passing an electric current between a cathode in the cathode chamber and an anode, to reduce the dissolved carbon dioxide to form a desired product.
2. The process of claim 1, wherein the gas (corrected to STP) to liquid volumetric feed ratio to the cathode chamber is greater than about 1.
3. The process of claim 1 or 2, wherein the effective superficial current density at the cathode is greater than  $1 \text{ kA/m}^2$ .
4. The process of claim 1, 2 or 3, wherein the carbon dioxide gas partial pressure in the cathode chamber is less than 10 Bar.
5. The process of any one of claims 1 to 4, wherein the electric current is a direct current driven by an electrochemical cell voltage.
6. The process of claim 5, wherein the electrochemical cell voltage is less than 10 Volts.
7. The process of any one of claims 1 to 6, wherein fluids in the cathode chamber are maintained at a cathode temperature above  $20^\circ \text{C}$ .
8. The process of any one of claims 1 to 7, wherein the cathode chamber is maintained at a cathode pressure and the cathode pressure is in the range of 1 Bar (100 kPa(abs)) to 10 Bar (1000 kPa(abs)).
9. The process of any one of claims 1 to 8, wherein the catholyte solvent is an aqueous solvent.
10. The process of claim 9, wherein the catholyte solvent comprises: a dissolved alkali metal bicarbonate or formate; or, a dissolved
11. The process of claim 9, wherein the bulk pH of the catholyte solvent is in the range of 4 to 10.
12. The process of claim 9, wherein the catholyte solvent comprises ammonium cations.
13. The process of any one of claims 1 to 12, wherein the cathode is a three dimensional electrode that has a thickness in the dimension of current flow of from 0.5 to 10 mm.
14. The process of claim 13, wherein the cathode has a porosity or voidage of from about 5% to about 95%.
15. The process of any one of claims 1 to 14, wherein the cathode comprises tin or lead.
16. The process of any one of claims 1 to 15, wherein the anode is in an anode chamber, and the anode chamber is separated from the cathode chamber by an electrochemical cell membrane.
17. The process of claim 16, wherein the anode chamber comprises an anolyte.
18. The process of claim 17, wherein the anolyte is an aqueous anolyte.
19. The process of claim 18, wherein the anolyte comprises:
- a) a dissolved alkali metal hydroxide;
- b) a dissolved alkali metal or ammonium salt;
- c) a dissolved acid, being  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , or  $\text{H}_3\text{PO}_4$ ;
- d) dissolved sulphuric acid and ammonium sulphate; or
20. The process of claim 18, wherein the anolyte comprises an ammonium ions.
21. The process of claim 16, wherein the electrochemical cell membrane is a cation permeable membrane.
22. The process of claim 16, wherein the electrochemical cell membrane permits selected ions to cross the membrane to balance the process stoichiometry.
23. The process of any one of claims 17 to 22, further comprising recycling at least a portion of the anolyte, the recycling anolyte, from an anolyte chamber outlet to an anolyte chamber inlet.
24. The process of claim 23, further comprising the step of separating an anode co-product from the recycling anolyte.
25. The process of any one of claims 17 to 24, further comprising Joule heating of the anolyte to provide heated anolyte.
26. The process of claim 25, further comprising Joule heating of the anolyte to provide heated anolyte, wherein the heated anolyte is used to heat the recycling catholyte solvent to separate water or the desired product from the recycling catholyte solvent by evaporation.
27. The process of any one of claims 1 to 26, wherein the desired product comprises a formate salt or formic acid.
28. The process of claim 27, wherein the formate salt is ammonium formate.
29. The process of any one of claims 1 to 28, further comprising separating the desired product from the catholyte solvent.
30. The process of any one of claims 1 to 28, further comprising recycling at least a portion of the catholyte solvent, the recycling catholyte solvent, from a cathode chamber outlet to a cathode chamber inlet.
31. The process of claim 30, further comprising the step of separating the desired product from the recycling catholyte solvent.
32. The process of claim 30, further comprising reacting recycling catholyte, comprising formate, with the anolyte, to obtain the desired product by an acidolysis reaction.
33. The process of claim 32, further comprising recycling at least a portion of the anolyte, the recycling anolyte, from an anolyte chamber outlet to an anolyte chamber inlet, and wherein the anolyte used to obtain the desired product is a portion of the recycling anolyte.

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