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(54) **Title:** METHOD AND REACTOR FOR ELECTROCHEMICALLY REDUCING CARBON DIOXIDE

(57) **Abstract:** The invention is directed to a method for electrochemically reducing carbon dioxide, and to an electrochemical reactor. The method of the invention for electrochemically reducing carbon dioxide, comprises a) introducing a water feed to an anode compartment of an electrochemical reactor, said anode compartment comprising an anode; b) introducing a carbon dioxide feed to a cathode compartment of an electrochemical reactor, said cathode compartment comprising a cathode; c) applying an electrical potential between the anode and the cathode in the electrochemical reactor sufficient for the cathode to reduce carbon dioxide into a reduced carbon dioxide product or product mixture, wherein said anode compartment is separated from said cathode compartment by a separator comprising a bipolar membrane, a charge-mosaic membrane, or a layered mixture of anion and cation exchange resins, preferably the separator comprises a bipolar membrane, and wherein the pressure in the electrochemical reactor is 20 bara or more.



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Title: METHOD AND REACTOR FOR ELECTROCHEMICALLY
REDUCING CARBON DIOXIDE

5 The invention is directed to a method for electrochemically
reducing carbon dioxide, and to an electrochemical reactor.

The combustion of fossil fuels in activities such as electricity
generation, transportation, and manufacturing produces billions of tons of
carbon dioxide annually. Increasing concentrations of carbon dioxide in the
10 atmosphere may be responsible for climate change, changing the pH of the
ocean and other potentially damaging effects. As a result, a lot of effort is
put in seeking ways to mitigate emissions of carbon dioxide.

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

At the moment, only a very minor fraction of carbon dioxide
20 emissions is actually used. As an end product of combustion, carbon dioxide
has a high thermodynamic stability, often demanding for an energy
intensive activation. Consequently, many processes for converting carbon
dioxide into useful end products are energy-intensive and/or dangerous.

An interesting alternative conversion process involves the
25 electrochemical reduction of carbon dioxide. Toxic or hazardous reducing
agents are then replaced by clean electrons. In this case, the high
thermodynamic stability of carbon dioxide is by-passed by a simple
one-electron reduction at an electrode, leading to *in situ* generation of
reactive intermediates. Often, room temperature conditions are sufficient,
30 considering that the energy of the electrons is determined by the applied
voltage. Since the electrochemical reduction takes place on a cathode

surface, the need for complex homogeneous organometallic catalysts is minimised. Furthermore, electricity will be increasingly of renewable origin in the future, making organic electro-synthesis a promising technology for environmentally friendly chemical processes. The electrochemical reduction
5 of carbon dioxide can be applied for the synthesis of fuels like formic acid, methanol or methane. This allows storage of electric energy from periodic sustainable origin, like solar or wind energy.

Electro-synthesis is typically carried out in an electrochemical reactor connected to an external voltage or current source. The
10 electrochemical reactors can be categorised into undivided and divided cells. A divided cell has a cathode compartment with a cathode, an anode compartment with an anode, and an interface (or divider or separator) between cathode compartment and anode compartment. The interface in a divided cell functions as a separator. It is a barrier for specific species while
15 allowing the transport of other species. The separator, for example, controls the flow of ions between the two compartments. In particular, the separator may selectively allow the transport of cations from the anode compartment into the cathode compartment while simultaneously preventing the transport of anions in the opposite direction. Alternatively, the separator
20 may selectively allow the transport of anions from the cathode compartment into the anode compartment while preventing the transport of cations in the opposite direction. Such control over ion flow provides a means to enhance or enforce the desired reaction chemistry to occur in the fluids contained in the individual compartments with respective electrodes, and increase the
25 current efficiency by preventing the cycling of species by sequential oxidation and reduction.

As mentioned above, the electrochemical reduction of carbon dioxide is a promising application in the field of electrochemistry. A variety of materials can be produced including formic acid, formates, carbon
30 monoxide, hydrogen, syngas, methanol, methane, and propane. Products

and process efficiencies depend amongst others on cell configuration, cathode material, surface area of the electrode, porosity of the electrode, catalyst, electrolyte (anolyte as well as catholyte) participating in reaction chemistry or acting as pH buffer, and process conditions like temperature,
5 pressure, applied fluid flow, (over)potential, *etc.*

A conventional configuration in the electrochemical reduction of carbon dioxide comprises a divided cell with a cation exchange membrane (proton exchange membrane or cation membrane) separating an aqueous anolyte and catholyte. Protons (from water splitting) and/or cations from the
10 specific anolyte, transfer to the cathode compartment where they react with the reduced carbon dioxide. Products formed are retained in the cathode compartment, while typically oxygen evolves at the anode. For example, US-A-2008/0 223 727 describes a continuous co-current electrochemical reduction of carbon dioxide using a catholyte mixture with a specific volume
15 ratio of carbon dioxide gas and liquid catholyte solvent.

In another reactor configuration a fuel like hydrogen is fed as a gas to the anode compartment. The protons, produced by direct splitting of the hydrogen fuel at the anode, transfer through the cation exchange membrane to react with the reduced carbon dioxide as in the previously
20 mentioned configuration.

In yet a further reactor configuration, an anion exchange membrane is employed as separator. The reduction of carbon dioxide at the cathode under wet conditions leads to the production of hydroxide ions that transfer through the anion exchange membrane and react with a hydrogen
25 fuel at the anode to produce water. The product of the carbon dioxide reduction is retained in the cathode compartment.

All the above reactor configurations have in common that they use an ion selective membrane of either the cation or the anion exchange type, and the use of an aqueous phase where at the cathode compartment carbon
30 dioxide is solubilised in the aqueous phase. Reduction and oxidation take

place in the cathode compartment and the anode compartment of the electrochemical reactor, respectively.

Bipolar membrane technology is relatively unexplored and finds an increasing number of applications in electro-catalytic membrane reactors (Balster *et al.*, *Chemical Engineering and Processing* 2004, 43, 1115-1127). A bipolar membrane is catalytically active and may contribute to electrochemical conversions. Bipolar membranes are known to be part of electro-dialysis stack design, and are configured together with anion and cation exchange membranes. A bipolar membrane is a synthetic membrane comprising two oppositely charged ion-exchanging layers in contact with each other. The bipolar membrane may be considered the combination of a cation exchange membrane and an anion exchange membrane. By this arrangement of charged layers, the bipolar membrane is not effective in transporting either cations or anions across the full width of the membrane, and is to be distinguished from the ion selective membranes employed in the conventional electrochemical reduction of carbon dioxide.

The use of a bipolar membrane in electrochemical reduction of carbon dioxide is known, however, from CN-A-102 912 374. This document describes the electrochemical reduction of carbon dioxide in an electrolytic tank comprising a cathode electrolysis compartment, catholyte, an anode electrolysis compartment, anolyte, and a bipolar membrane for dividing the cathode electrolysis compartment and the anode electrolysis compartment. The electrochemical electrolytic reduction of carbon dioxide in this document, indicating the use of anolyte and catholyte, implies ambient temperature and pressure.

While a process for the electrochemical reduction of carbon dioxide at elevated pressure is known *e.g.* from WO-A-2014/043651 and US-A-2013/0 105 304, in these processes the carbon dioxide is dissolved in water, which does not allow for the carbon dioxide densities in the reactor as achieved in the present invention. Consequently, these processes at elevated

pressure but based on an aqueous solution also require the use of an electrolyte. In the present invention, carbon dioxide is the main reaction medium (the solvent) and a small fraction of water is added to form ionic reaction species at the cathode side. These ionic reactive species assure electric conductivity and will (simultaneously) participate in the overall reduction reaction of carbon dioxide. These two aspects (conductivity and participation in the reaction) assure a minimal use, or no use at all, of an electrolyte/catholyte solution.

Problems associated with the conventional electrochemical processes include low availability of gaseous reactant at atmospheric pressure, substantial over potentials at the electrodes (stack), a high internal resistance to overcome (low power density), co-transport of anolyte with protons through cation exchange membrane and competitive reaction of these with the anion in the cathode compartment and a requirement for a secondary chemical conversion outside the main electrochemical reactor, low water dissociation rate, difficulties in achieving full conversion of a liquid and a gaseous reactant in a single pass through an electrochemical reactor operated in continuous mode, integrity of a thin membrane during pressurisation or depressurisation in particular with a gaseous phase on one side and a liquid phase on the other side.

Objective of the invention is to overcome one or more of these problems faced in the prior art.

The inventors surprisingly found that this objective can, at least in part, be met by employing a specific type of separator that participates in the reaction chemistry.

Accordingly, in a first aspect the invention is directed to a method for electrochemically reducing carbon dioxide, comprising

a) introducing a water feed to an anode compartment of an electrochemical reactor, said anode compartment comprising an anode;

b) introducing a carbon dioxide feed to a cathode compartment of an electrochemical reactor, said cathode compartment comprising a cathode;
c) applying an electrical potential between the anode and the cathode in the electrochemical reactor sufficient for the cathode to reduce carbon dioxide
5 into a reduced carbon dioxide product or product mixture,
wherein said anode compartment is separated from said cathode compartment by a separator comprising a bipolar membrane, a charge-mosaic membrane, or a layered mixture of anion and cation exchange resins, and wherein the pressure in the electrochemical reactor is
10 20 bara or more.

In accordance with the method of the invention, the separator participates in the intended reaction chemistry instead of only transferring either cations or anions as being state of the art in carbon dioxide electrochemical reduction employing a cation exchange membrane or an
15 anion exchange membrane, respectively. The method of the invention advantageously allows for high electric power density, low voltage over-potentials and a low internal resistance for electricity/electric current, a reactive layer with potential high services for direct gas/dense phase and liquid/supercritical phase conversion of carbon dioxide, a tremendously
20 increased dissociation rate of water into H^+ and OH^- in the separator as compared to the equilibrium dissociation rate of water, production of OH^- at the internal interface in the membrane as compared to production at the anode, versatility to operate the electrochemical reactor in continuous, as well as in semi-continuous or batch mode, and prevention of mechanical
25 rupture or leakage of the membrane during start up or shut down of the reactor.

Without wishing to be bound by any theory, the inventors believe that in accordance with the invention the reduction of carbon dioxide occurs in a reaction volume wherein the concentration of reactive species is

exceptionally high. The result is a highly efficient conversion, wherein a very pure product can be obtained in one single production step.

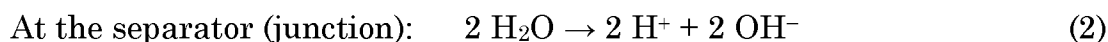
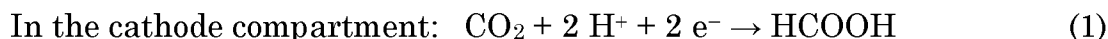
The separator can comprise (or consist of) a bipolar membrane, a charge-mosaic membrane, or a layered mixture of anion and cation exchange resins. A bipolar membrane is defined as a synthetic membrane comprising two oppositely charged ion-exchanging layers in contact with each other. A charge-mosaic membrane is defined as a membrane having a charge structure comprised of cation-exchange domains and anion-exchange domains which are alternately aligned and each of which penetrates the membrane from one side to the other side. The separator may also be a permeable layer confining a mixture of a cation exchange resin and an anion exchange resin. Preferably, the separator comprises or consists of a bipolar membrane.

The separator may be in direct electrical contact with the cathode and/or anode of the electrochemical reactor. Alternatively, the separator may be in indirect electrical contact with the cathode and/or anode of the electrochemical reactor via an electrically conductive liquid, such as an electrolyte, or more specifically a catholyte or anolyte.

The method of the invention may be performed in various embodiments that allow reduction of carbon dioxide using different configurations of the electrochemical reactor.

For example, water can be split at the separator, thereby producing OH^- ions and H^+ ions. The feed with carbon dioxide (which can be present in different forms such as carbon dioxide, carbonic acid, bicarbonate, carbonate, *etc.*) can be reduced in the cathode compartment while consuming the H^+ ions, and the OH^- ions can be oxidised in the anode compartment between to produce water. In this example, the separator preferably comprises a cation exchange layer and an anion exchange layer in contact with each other at a junction, wherein the cation exchange layer faces the cathode and the anion exchange layer faces the anode.

This configuration may be represented by the following overall reactions.



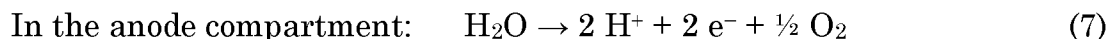
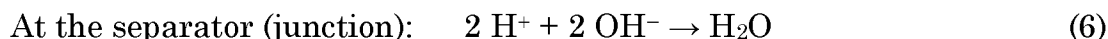
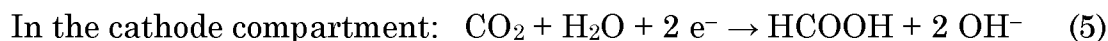
The net result of these three reactions is:



This exemplary configuration is shown in figure 1, wherein an electrochemical reactor 100 comprises a cathode compartment 110, a separator 120, and an anode compartment 130.

In another example, carbon dioxide can be reduced in the cathode compartment (where the carbon dioxide can be present in different forms such as carbon dioxide, carbonic acid, bicarbonate, carbonate, *etc.*), thereby producing OH^- ions. In the anode compartment, water can be oxidised to produce H^+ ions. The OH^- ions and H^+ ions can be recombined at the separator, thereby producing water. In this example, the separator preferably comprises a cation exchange layer and an anion exchange layer in contact with each other at a junction, wherein the anion exchange layer faces the cathode and the cation exchange layer faces the anode.

20 This configuration may be represented by the following overall reactions.



25 The net result of these three reactions is:



This exemplary configuration is shown in figure 2, wherein an electrochemical reactor 100 comprises a cathode compartment 210, a separator 220, and an anode compartment 230.

Hence, depending on the configuration of the electrochemical reactor, different electrochemical conversions can be performed with the method of the invention. In one embodiment, the separator comprises a cation exchange layer and an anion exchange layer in contact with each other at a junction, wherein the cation exchange layer faces the cathode and the anion exchange layer faces the anode. In a further embodiment, the separator comprises a cation exchange layer and an anion exchange layer in contact with each other at a junction, wherein the anion exchange layer faces the cathode and the cation exchange layer faces the anode.

The electrochemical reactor can advantageously be free of liquid electrolyte, such as catholyte and/or anolyte. Preferably, the electrochemical reactor is free of catholyte. The cathode and bipolar membrane can be in direct contact in order to minimise electrical resistance. Carbon dioxide can, for example be supplied as dense gas to the cathode compartment, and water may be supplied either to the cathode compartment or to the anode compartment in the appropriate amount to wet the cathode and anode structure thereby forming a reactive layer. The absence of liquid electrolyte is highly preferred, as the presence of liquid electrolyte can lead to the production of undesirable by-products.

The method may be operated continuously, semi-continuously, or in batch. It is preferred to perform the method of the invention in a continuous mode.

Preferably, the method of the invention further comprises releasing oxygen from the anode compartment, and collecting reduced carbon dioxide product or product mixture from the cathode compartment.

The reduced carbon dioxide product or product mixture can comprise one or more components from a group of molecules referred to as platform chemicals, such as alkanes, alkenes, syngas, carboxylic acids, alcohols, including diols, aldehydes, and ketones. More specifically, the carbon dioxide product or product mixture can comprise one or more

components selected from the group consisting of carbon monoxide, hydrogen, syngas, formic acid, a formate, methanol, acetaldehyde, methane, and ethane. Preferably, the reduced carbon dioxide or product mixture comprises one or more selected from the group consisting of methanol, formic acid, a formate, and acetaldehyde. Accordingly, the method can involve the conversion of carbon dioxide into one or more of these compounds. In a preferred embodiment, the method comprises the conversion of carbon dioxide to formic acid. The product that is obtained may be controlled by varying the applied voltage.

10 A water feed is introduced into the anode compartment. This water feed may be supplied in liquid form, in vapour form or in gaseous form. The water feed comprises at least water, but may further comprise other components such as one or more selected from the group consisting of pH control agents, conductivity control agents, and reactivity inhibitors. It is also possible that the water feed is water. Suitably, the water feed is a feed that has water as main component.

 A carbon dioxide feed is introduced into the cathode compartment. This carbon dioxide feed may be supplied in one of the following phase, as a supercritical phase, in a liquid phase, in a dense phase, in a vapour phase or in a gaseous phase. Preferably, the carbon dioxide feed is in a dense phase. As is commonly known in the art, dense phase carbon dioxide refers to carbon dioxide in either liquid form or supercritical form. In the case of a liquid, the carbon dioxide itself may be liquid, or it may be a solute in a liquid solvent, such as water. The carbon dioxide feed comprises at least carbon dioxide, but may further comprise other components, such as one or more selected from the group consisting of water droplets, aerosols, pH control agents, conductivity control agents, and compounds for mediated electrochemical conversion. Suitably, the carbon dioxide feed is a feed that has carbon dioxide as main component. Preferably, the carbon dioxide feed comprises a majority of carbon dioxide and a minority of water.

It is preferred that the carbon dioxide feed is pre-conditioned in a dedicated vessel to obtain high concentrations of reactive species (CO_2 , carbonic acid, bicarbonate, and carbonate) for carbon dioxide reduction. The carbon dioxide feed is suitably pre-conditioned in terms of pressure, temperature, and pH, and preferably consists of a mixture of carbon dioxide and water with an excess of carbon dioxide. With respect to the pressure, the carbon dioxide is preferably fed to the reactor in a dense phase and water is preferably partly solubilised in the dense carbon dioxide phase, whereby the dense phase carbon dioxide will be highly concentrated with ionic reactive species. These reactive species are formed by a reaction between water and the carbon dioxide during the pre-conditioning step, and (additional) ionic reactive species can be formed during the contacting in the electrochemical reactor of the dense phase carbon dioxide with the membrane where the membrane is saturated with water.

The pressure of the carbon dioxide feed is preferably 20 bara or more, such as 30 bara or more, even more preferably 50 bara or more, and most preferably 60 bara or more. Usually, the pressure of the carbon dioxide feed will not exceed 200 bara. More preferably, the pressure of the carbon dioxide feed will be 150 bara or less, even more preferably 100 bara or less, and most preferably 80 bara or less.

The carbon dioxide feed may have a density of 10-1000 kg/m^3 , preferably a density of 100-980 kg/m^3 , and more preferably a density of 600-960 kg/m^3 .

Both water feed and carbon dioxide feed may be introduced into the electrochemical reactor continuously or intermittently. It is also possible to introduce the water feed and carbon dioxide feed into the electrochemical reactor in a batch wise fashion.

While reduced carbon dioxide product or product mixture is produced in the cathode compartment, typically oxygen is produced in the anode compartment. This oxygen can be released from the anode

compartment via an anode compartment outlet. It is preferred that the rate of introducing the carbon dioxide feed and the rate of releasing the oxygen is monitored and controlled. This may be realised, for instance, by releasing oxygen when the absolute pressure thereof is 0.2 bar or more higher than the pressure of the carbon dioxide feed, preferably 0.3-1.0 bar higher than the pressure of the carbon dioxide feed, and more preferably 0.4-0.8 bar higher than the pressure of the carbon dioxide feed. This control can advantageously prevent mechanical damages by avoiding large pressure differences in the system.

In another configuration, the pressure difference between the anode and the cathode compartment, *i.e.* the pressure difference over the membrane, will be used to control the rate of introducing the carbon dioxide feed and releasing the oxygen. The oxygen may be released, for instance, when the pressure difference between the anode and the cathode compartment is 0.2 bar or more, preferably in the range of 0.2-1.0 bar pressure difference, and more preferably in the range of 0.3-0.8 bar pressure difference.

This control of the feeding and the release of the various streams can be achieved, by an advanced pressure control system, employing pressure transducers, pressure transmitters, pressure controllers, and pressure differential transducers.

For example, the carbon dioxide feed can be fed to the electrochemical reactor at a fixed pressure (*e.g.* in the range of 20-100 bara), thereby guaranteeing an automatic supplementation of this reactant.

Fluctuations in the water feed can be damped by using, for example, an expansion chamber, pusher bellows, *etc.* In the preferred configuration, for both the water feed stream and the carbon dioxide feed stream a (pre)conditioning step is included. Preferably, for each stream a pressurised, thermostatic vessel or hydraulic accumulator is employed to assure stable pressure and temperature levels for the feed streams. A basic process flow

diagram of the main process steps including the most relevant instrumentation for pressure control is depicted in figure 3.

The water feed supplied at the anode can be in direct contact with the produced gaseous oxygen. The pressure thereof can be at an absolute
5 pressure with a set-point for a control valve to release oxygen slightly higher than the carbon dioxide feed pressure, for example 0.5 bar higher than the carbon dioxide feed pressure. For the different modes of operation, batch semi-batch and continuous operation, the pressure difference over the membrane and the pressure difference between the various streams (water,
10 carbon dioxide and oxygen) will not exceed the pressure of the operational window. Preferably, the pressure difference over the membrane should be in the range of 0.3-0.8 bar.

The command signal for the valve can be derived from a sensor that monitors an absolute pressure. Preferably the liquid reactants contact
15 the pressure hull of the vessel.

During start-up, shutting down, or in emergency situations, distinct or even abrupt pressure differences may occur between the anode compartment and the cathode compartment. In order to avoid any problems related with such pressure differences, a sensor may be employed that
20 monitors a pressure differential between the carbon dioxide feed and released oxygen and controls and overrules the absolute pressure signal command. The pressure differential signal can affect the operation of a valve connected to the cathode compartment inlet to adjust the rate of carbon dioxide feed introduction and a valve at the anode compartment
25 outlet to adjust the rate of oxygen release. The discharge rate of the reduced carbon dioxide product or product mixture may be controlled using a control valve connected to the cathode compartment outlet.

The pressure in the electrochemical reactor is 20 bara or more, preferably 30 bara or more, even more preferably 50 bara or more, and most
30 preferably 60 bara or more. Usually, the pressure in the electrochemical

reactor will not exceed 200 bara. More preferably, the pressure in the electrochemical reactor will be 150 bara or less, even more preferably 100 bara or less, and most preferably 80 bara or less.

In a particular embodiment, an overpressure is maintained in the anode compartment with respect to the cathode compartment. The separator divides the reactor in two compartments, wherein the anode compartment suitably contains a liquid phase (such as an aqueous liquid), while the cathode compartment suitably contains a gaseous phase (such as a carbon dioxide gas). Typically, the liquid phase is difficult to compress, while the gaseous phase can be more easily compressed. Possible pressure fluctuations that may occur in the system could lead to transport of the liquid through the membrane in the direction of the gaseous phase. In order to prevent this from happening, it is preferred to employ a small overpressure, with the bipolar membrane preferably supported at least at the interface with the cathode compartment. Moreover, this overpressure can facilitate the diffusion of H^+ ions in the bipolar membrane. The over-pressure can, for example, be in the range of 0.2-0.5 bar, such as 0.3-0.4 bar.

The reduced carbon dioxide product or product mixture can be further purified after being collected using one or more of the state of the art separation methods, such as distillation, absorption or membrane separation.

Such purification may comprise one or more from the group of membrane separations consisting of ultrafiltration, nanofiltration, pervaporation, vapour permeation, and membrane distillation. Such purification methods can be based on the difference in molecular size and/or affinity for a membrane material.

In an embodiment, the method comprises a step wherein the reduced carbon dioxide product or product mixture is subjected to

dehydration. Such dehydration may, for instance, involve dehydration of methanol and/or acetaldehyde.

The residual or permeate of a purification step of the reduced carbon dioxide product or product mixture can optionally be recycled to the
5 carbon dioxide feed, optionally after recompression.

The temperature in the electrochemical reactor during the method of the invention is preferably 20 °C or less, and may be even cooler, such as 10 °C or less, or even 5 °C or less. The temperature will normally not be below 0 °C. Such relatively low temperatures can be achieved by
10 active cooling of the electrochemical reactor and/or by introducing low temperature water feed and/or low temperature carbon dioxide feed (*e.g.* by active cooling of the feed).

The reduced carbon dioxide product or product mixture can be collected. This may be accomplished by removing reduced carbon dioxide
15 product or product mixture from the cathode compartment via a cathode compartment outlet. Such outlet is typically located at the bottom of the cathode compartment. The product or product mixture can then suitably be collected in a separate volume, before optionally being processed further.

The electrical potential between the anode and the cathode can be
20 applied using an external power supply that is connected to the electrodes (anode and cathode). The electrical potential should be sufficient to drive the reaction, and more in particular for the cathode to reduce carbon dioxide into a reduced carbon dioxide product or product mixture.

In a further aspect, the invention is directed to an electrochemical
25 reactor, preferably for performing a method as described herein, said reactor comprising an anode compartment separated from a cathode compartment by a separator, wherein said cathode compartment is in contact with a cathode and said anode compartment is in contact with an anode, said anode compartment comprising an anode compartment inlet for feeding
30 water and an anode compartment outlet for releasing oxygen,

said cathode compartment comprising a cathode compartment inlet for feeding carbon dioxide and a cathode compartment outlet for collecting reduced carbon dioxide product or product mixture, wherein said separator is selected from the group consisting of a bipolar membrane, a charge-mosaic membrane, and a layered mixture of anion and cation exchange resins, said electrochemical reactor being configured to operate at a pressure of 20 bara or more.

The cathode and/or the anode may be embedded in the separator. For example, in case of a bipolar membrane, the cathode and/or anode may be embedded in one of the ion exchange layers of the bipolar membrane. In such a case, the cathode is preferably embedded in one of the ion exchange layers, and the anode is embedded in the other ion exchange layer.

The separator preferably comprises a cation exchange layer and an anion exchange layer. The separator can then be oriented in the electrochemical reactor such that the cation exchange layer faces the cathode and the anion exchange layer faces the anode. Alternatively, the separator can be oriented in the electrochemical reactor such that the anion exchange layer faces the cathode and the cation exchange layer faces the anode.

Preferably, the electrochemical reactor is configured to operate at a pressure of 20 bara or more, more preferably 30 bara or more, even more preferably 50 bara or more, such as 60 bara or more. Usually, the pressure in the electrochemical reactor will not exceed 200 bara. The pressure in the electrochemical reactor is preferably 150 bara or less, more preferably 100 bara or less, such as 80 bara or less.

In order to improve the mechanically properties of the reactor, the separator may be mechanically supported on at least one side. It is also possible to mechanically confine the separator between two mechanical supports. The reactor can further be mechanically supported by a holder, which may hold the mechanical support.

The reactor can suitably further comprise a water feed line, a carbon dioxide feed line, an oxygen release line, and a reduced carbon dioxide product collection line. The water feed line is then connected to the anode compartment inlet, the carbon dioxide feed line is then connected to the cathode compartment inlet, the oxygen release line is then connected to the anode compartment outlet, and the reduced carbon dioxide product collection line is then connected to the cathode compartment outlet. Suitably, the oxygen release line and/or the anode compartment inlet comprises a pressure valve which is operably linked to a pressure sensor for measuring the pressure difference between the carbon dioxide feed line and the oxygen release line. Separately or additionally, the carbon dioxide feed line and/or the cathode compartment inlet may comprise a pressure valve which is operably linked to a pressure sensor for measuring the pressure difference between the carbon dioxide feed line and the oxygen release line. The pressure valve at the oxygen release side may further be operably linked to a pressure sensor for measuring the absolute pressure in the oxygen release line. Hence, the system pressure can be controlled by venting the released oxygen, while the differential pressure can be maintained at the appropriate level by controlling the carbon dioxide feed. As such, the system will be balanced.

In a further aspect the invention is directed to a electrochemical reaction module, comprising two or more electrochemical reactors as described herein in parallel.

For example, a stack of repeat units (300) as shown in figure 4a may be placed in a high pressure reaction vessel as shown in figure 4b. The repeat unit (300) shown in figure 4a contains a bipolar membrane (100) confined between two constructive parts of similar design that form the cathode compartment and the anode compartment, respectively. Each part consists of a holder (320) for conductive mechanical support (310). The cathode compartment has a port (330) opening to a common cathode feed

volume. The anode compartment has a port (340) opening to a common anode feed volume. Figure 4b shows a stack of the repeat units (300) in a high pressure reaction vessel. In this example, the high pressure vessel consists of two parts. The upper part (420) is only a cover and can be removed for access to the electrodes and membranes. The lower part (410) supports the stack of cathode-bipolar membrane-anode repeat units, which physically separates the cathode compartment of the reactor vessel at the bottom of the reactor vessel from the anode compartment of the reactor vessel at the top of the reactor vessel. The lower part has two entry ports; one for the cathode feed (430), for example carbon dioxide at high pressure, and for the anode feed (440), for example water. The lower part has two exit ports; one for the reaction product(s) at the cathode side (450), and one for the anode side (460). The tubing connected to entry and exit ports can be brought to the desired level inside the high-pressure electrochemical reactor vessel. The lower part of the reactor vessel also contains the connection ports to a differential pressure sensing device (470). Albeit not shown, it is clear that pressure sensing devices for sensing cathode compartment pressure and/or anode compartment pressure can be mounted on the lower part of the reactor vessel.

In accordance with the invention, a number of such high pressure reaction vessels may, for instance, be operated in parallel. An example thereof is shown in figure 3. In this example, water (1) and carbon dioxide (2) feeds are fed to respectively the anode and the cathode chambers of the high pressure reaction vessel. The product mixture (3) is collected at the bottom of the reaction and is purified in a separation unit. The product (4) (here formic acid), leaves the system. Oxygen (5) evolves at the anode and leaves the system as a gas from the anode chamber. The permeate of the separation unit (10), is recompressed and recycled into the dense carbon dioxide feed stream (2).

A further example of an electrochemical reactor is shown in figure 5. In this example, the reactor (500) contains a bipolar membrane (100) in a cylindrical configuration. The bipolar membrane has a mechanical support (510). This mechanical support allows a dense gas phase reactant (*e.g.* carbon dioxide, or carbon dioxide plus water vapour at high pressure) to pass from the cathode compartment. The product is collected in to the cathode compartment volume (530). At the other side of the bipolar membrane is a conductive screen (520) that allows a liquid phase reactant (such as water or water plus electrolyte) to pass from the anode compartment. The anode chamber is in open contact with the common anode chamber volume (540). A stack of these electrochemical reactors (500) may be placed in a high pressure reaction vessel, for example in a similar fashion as shown in figure 4b, or as a single unit in a high pressure tube, the aggregate being a tube-in-tube electrochemical reactor.

All references cited herein are hereby completely incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

The use of the terms “a” and “an” and “the” and similar referents in the context of describing the invention (especially in the context of the claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms “comprising”, “having”, “including” and “containing” are to be construed as open-ended terms (*i.e.*, meaning “including, but not limited to”) unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. The use of any and all examples, or exemplary language (*e.g.*, “such as”) provided herein, is intended merely to better illuminate the

invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention. For the purpose of the description and of the appended claims, 5 except where otherwise indicated, all numbers expressing amounts, quantities, percentages, and so forth, are to be understood as being modified in all instances by the term "about". Also, all ranges include any combination of the maximum and minimum points disclosed and include and intermediate ranges therein, which may or may not be specifically 10 enumerated herein.

Preferred embodiments of this invention are described herein. Variation of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, 15 and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject-matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is 20 encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context. The claims are to be construed to include alternative embodiments to the extent permitted by the prior art.

For the purpose of clarity and a concise description features are described herein as part of the same or separate embodiments, however, it 25 will be appreciated that the scope of the invention may include embodiments having combinations of all or some of the features described.

The invention will now be further illustrated by the following non-limiting example.

Examples

A high pressure electrochemical cell was designed in order to have optimal dimensions for the reactor. This is, in particular, relevant for the volume of the electrolyte compartments, the surface area of the membrane, and the surface area of the electrodes. The operating conditions are, typically, in the range of 1-100 bar and temperatures are in the range of 5-50 °C.

The use of a high pressure, dense phase mixture of carbon dioxide and water has as main advantage that high concentrations of ionic, reactive species especially, bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) will be formed. The presence of the ionic carbonate species (HCO_3^- and CO_3^{2-}) avoids the need of using an additional electrolyte solution. More specifically, in the proposed reactor configuration there is no need to use a catholyte and/or anolyte solution.

Table 1 shows the amount of CO_2 (concentration of CO_2 per litre) when CO_2 is solubilised in water up to a pressure of 10 bar. In this case the CO_2 concentration is also referred to as the CO_2 solubility. Table 2 shows the maximum amount (concentration of CO_2 per litre) that can be achieved at the given conditions in the case where a small amount of water is added to a CO_2 dense phase. For the two situations a temperature of 20 °C is taken, which might require some cooling of the reactor.

Table 1: Concentration of CO_2 for different conditions, starting with an aqueous solution.

CO_2 in water	
<i>conditions</i>	<i>maximum CO_2 concentration</i>
p = 1 bar, T = 20 °C	1.4 g CO_2/l
p = 10 bar, T = 20 °C	12.5 g CO_2/l

Table 2: Concentration (based on density) of CO₂ for different conditions, starting with a dense CO₂ phase.

Binary mixture of (dense) CO ₂ and water	
<i>conditions</i>	<i>maximum CO₂ concentration</i>
p = 10 bar, T = 20 °C	19 g CO ₂ /l
p = 50 bar, T = 20 °C	140 g CO ₂ /l
p = 100 bar, T = 20 °C	850 g CO ₂ /l

Based on the use of a high pressure, dense CO₂ phase and the absence of an electrolyte solution, a relatively small reaction volume can be used, as compared to the conventional electrochemical cells that employ an electrolyte solution. In a conventional electrochemical cell, the typical conditions that are applied are atmospheric pressures, and as a result the mass-based ratio of the reactant CO₂, to be consumed in the reduction reaction, to the water (in the electrolyte solution) is well below unity. For a typical electrochemical cell the mass-based CO₂ to water ratio is in the order of 0.001-0.005 (1 to 5 g CO₂ per litre water). While in the case of starting with a dense phase CO₂, the envisaged CO₂ to water (mass-based) ratio will be close to unity, based on densities and operation above 50 bar and temperatures below 20 °C.

A small reaction volume assures a small(er) distance between the electrodes and the bipolar membrane, with as main result a minimal resistance for the electrical current, and the optimal (minimum) ratio of reaction volume to electrode surface area also assures a high current density. Furthermore, because of the difference in density between the dense CO₂ phase and the liquid formic acid phase, with a density of formic acid of 1.22 kg/l there will be a separation of the product from the reactants.

In the absence of an (extra) electrolyte solution no unwanted side reactions, with species typically present in the electrolyte solution, will occur, and therefore in the proposed reactor configuration the selectivity

towards the desired product will be increased. Furthermore, no significant change in pH value occurs as a result of the high concentration of bicarbonate and carbonate species.

In addition, the use of the bipolar membrane will assure a high
 5 flux of (only) protons (hydrogen ions, H^+ ions) across the membrane into the dense CO_2 phase. The use of the bipolar membrane for the water splitting, into OH^- and H^+ , is an essential step for high selective reduction of carbon dioxide. with a bipolar membrane only hydrogen ions will flow into the dense CO_2 phase with the bicarbonate and carbonate ions. Again, the
 10 absence of additional ions that are normally exchanged across ion exchange membranes used in electro-catalytic reduction of CO_2 will assure no unwanted side reactions.

The reactor configuration is ideally suited for the production of formic acid, by providing flexible operation to achieve the required and
 15 selected over-potential for carbon dioxide reduction, according to the following reactions/steps:

- high pressure mixing of water in dense CO_2 phase



- equilibrium and formation of (bi)carbonate species by solvation



- water splitting



- main reaction



25 The overall reaction for the direct electrochemical conversion of CO_2 to formic acid is then as follows.



Based on the (starting) amount of CO_2 in a reactor volume of 1 l (1000 ml) as given in table 1 and table 2, the following concentrations for formic acid can
 30 be obtained, see case 1 and case 2 below. From the molar mass it follows

that about 1 gram of CO₂ (MW = 44.00 g/mol) gives about 1.05 gram of formic acid (MW = 46.03 g/mol). For the formation of formic acid from CO₂ a current efficiency of around 80 % has been reported, the density of formic acid is 1.22 g/ml, for water a density of 1 g/ml is taken.

5

Case 1:

Starting with a dense phase mixture of 500 ml CO₂ and 500 ml water, using a reactor volume of 1 l (1000 ml), at 100 bar and 20 °C gives: $(500 / 1000) * 850 = 425$ g CO₂, which yields: $(0.8 * 1.05 * 425 =)$ 357 g of formic acid.

10

For the concentration in vol.%, and after the pressure has been reduced this gives: $(357 * 1.22 =)$ 436 ml or 42.6 vol.% formic acid.

Case 2:

15

Starting with an aqueous solution at 10 bar and 20 °C, the amount of CO₂ is 12.5 g/l, which is a factor of $(425 / 12.5 =)$ 34 lower than for case 1 which uses a dense phase. This corresponds to a formic acid concentration of $(43.6 / 34 =)$ 1.3 vol.%.

20

For an aqueous system at 1 bar and 20 °C, the amount of CO₂ is a factor $(425 / 1.4 =)$ 304 lower, resulting in a (maximum) formic acid concentration of $(42.6 / 304 =)$ 0.14 vol.%.

Claims

1. Method for electrochemically reducing carbon dioxide, comprising
 - a) introducing a water feed to an anode compartment of an electrochemical reactor, said anode compartment comprising an anode;
 - b) introducing a carbon dioxide feed to a cathode compartment of an
 - 5 electrochemical reactor, said cathode compartment comprising a cathode;
 - c) applying an electrical potential between the anode and the cathode in the electrochemical reactor sufficient for the cathode to reduce carbon dioxide into a reduced carbon dioxide product or product mixture,wherein said anode compartment is separated from said cathode
- 10 compartment by a separator comprising a bipolar membrane, a charge-mosaic membrane, or a layered mixture of anion and cation exchange resins, and wherein the pressure in the electrochemical reactor is 20 bara or more.
- 15 2. Method according to claim 1, wherein the separator comprises a bipolar membrane.
3. Method according to claim 1 or 2, wherein the carbon dioxide feed is pre-conditioned in terms of one or more selected from the group consisting
- 20 of pressure, temperature, and pH, preferably in terms of each of those
4. Method according to any one of claims 1-3, wherein the carbon dioxide feed comprises a majority of carbon dioxide and a minority of water.
- 25 5. Method according to any one of claims 1-4, wherein the carbon dioxide feed is above atmospheric pressure.

6. Method according to any one of claims 1-5, wherein the carbon dioxide feed has a pressure of 20 bara or more, preferably 30 bara or more, more preferably 50 bara or more, such as 60 bara or more.

5 7. Method according to any one of claims 1-6, wherein the carbon dioxide feed has a density of 10-1000 kg/m³, preferably 100-980 kg/m³, more preferably 600-960 kg/m³.

8. Method according to any one of claims 1-7, wherein said
10 electrochemical reactor is free of liquid electrolyte.

9. Method according to any one of claims 1-8, said method comprising

- splitting water at the separator, thereby producing OH⁻ ions and H⁺ ions,
- 15 - reducing carbon dioxide in the cathode compartment, thereby consuming said H⁺ ions, and
- oxidising said OH⁻ ions in the anode compartment to produce water.

10. Method according to claim 7, wherein said separator comprises a
20 cation exchange layer and an anion exchange layer in contact with each other at a junction, and wherein the cathode exchange layer faces the cathode and the anion exchange layer faces the anode.

11. Method according to any one of claims 1-8, said method
25 comprising

- reducing carbon dioxide in the cathode compartment, thereby producing OH⁻ ions, and
- oxidising water in the anode compartment to produce H⁺ ions, and
- recombining said OH⁻ ions and H⁺ ions at the separator to produce water.

12. Method according to claim 11, wherein said separator comprises a cation exchange layer and an anion exchange layer in contact with each other at a junction, and wherein the anode exchange layer faces the cathode and the cation exchange layer faces the anode.

5

13. Method according to any one of claims 3-12, wherein the carbon dioxide feed is pre-conditioned in a form selected from the group consisting of carbon dioxide, carbonic acid, bicarbonate, and carbonate, preferably in the form of bicarbonate

10

14. Method according to any one of claims 1-13, wherein the carbon dioxide feed is in the form of a supercritical phase, a dense phase, a liquid phase, or gas phase.

15. Method according to any one of claims 1-14, wherein said method is operated continuously and comprises

- releasing oxygen from the anode compartment, and
- collecting reduced carbon dioxide product or product mixture from said cathode compartment.

20

16. Method according to any one of claims 1-15, wherein said method involves the conversion of carbon dioxide into one or more platform molecules selected from the group consisting of syngas, alkanes, alkenes, alcohols including diols, carboxylic acids, aldehydes, and ketones.

25

17. Method according to any one of claims 1-16, wherein the method involves the conversion of carbon dioxide into one or more selected from the group consisting of carbon monoxide, hydrogen, syngas, formic acid, a formate, methanol, acetaldehyde, methane, and ethane.

30

18. Method according to any one of claims 1-17, wherein the pressure in the electrochemical reactor is 30 bara or more, preferably 50 bara or more, such as 50-200 bara.
- 5 19. Method according to any one of claims 1-18, wherein said reduced carbon dioxide product or product mixture is purified, preferably by one or more from the group consisting of ultrafiltration, nanofiltration, pervaporation, vapour permeation and membrane distillation.
- 10 20. Method according to any one of claims 15-19, wherein the rate of introducing said carbon dioxide feed and the rate of releasing said oxygen is monitored and controlled.
- 15 21. Method according to any one of claims 15-20, wherein oxygen is released when the absolute pressure thereof is 0.2 bar or more higher than the pressure of the carbon dioxide feed, preferably 0.3-1.0 bar higher than the pressure of the carbon dioxide feed, more preferably 0.4-0.8 bar higher than the pressure of the carbon dioxide feed.
- 20 22. Method according to any one of claims 1-21, wherein an overpressure is maintained in the anode compartment with respect to the cathode compartment
- 25 23. Method according to claim 22, wherein said overpressure, indicated as a pressure difference, is in the range of 0.3-0.5 bar mbar, preferably in the range of 0.2-0.4 bar.
- 30 24. Electrochemical reactor, preferably for performing a method according to any one of claims 1-23, said reactor comprising an anode compartment separated from a cathode compartment by a separator,

wherein said cathode compartment is in contact with a cathode and said anode compartment is in contact with an anode, said anode compartment comprising an anode compartment inlet for feeding water and an anode compartment outlet for releasing oxygen, said cathode compartment
5 comprising a cathode compartment inlet for feeding carbon dioxide, and a cathode compartment outlet for collecting reduced carbon dioxide product or product mixture, wherein said separator is selected from the group consisting of a bipolar membrane, a charge-mosaic membrane, and a layered mixture of anion and cation exchange resins,
10 said electrochemical reactor being configured to operate at a pressure of 20 bara or more.

25. Electrochemical reactor according to claim 24, wherein the cathode and/or the anode is/are embedded in the separator.

15

26. Electrochemical reactor according to claim 24 or 25, wherein the separator comprises a cation exchange layer and an anion exchange layer and wherein the separator is oriented such that the cation exchange layer faces the cathode and the anion exchange layer faces the anode.

20

27. Electrochemical reactor according to claim 24 or 25, wherein the separator comprises a cation exchange layer and an anion exchange layer and wherein the separator is oriented such that the cation exchange layer faces the anode and the anion exchange layer faces the cathode.

25

28. Electrochemical reactor according to any one of claims 24-27, wherein the separator is mechanically supported on at least one side, or is confined between two mechanical supports.

29. Electrochemical reactor according to any one of claims 24-28, said reactor further comprising a water feed line, a carbon dioxide feed line, an oxygen release line, and a reduced carbon dioxide product collection line, wherein oxygen release line comprises a pressure valve which is operably
- 5 linked to a pressure sensor for measuring the pressure difference between the carbon dioxide feed line and the oxygen release line.

Figure 1

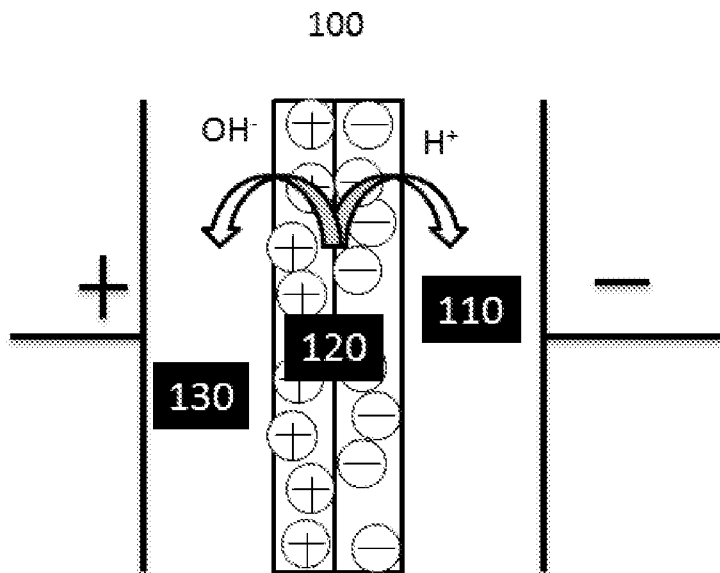
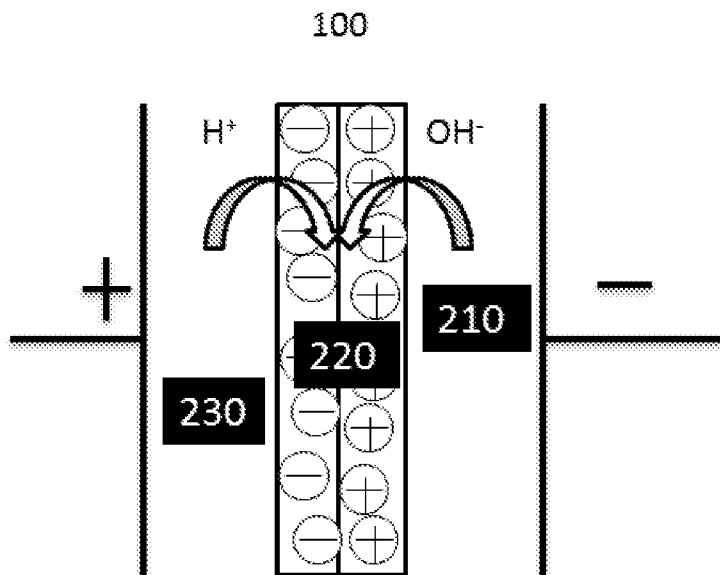


Figure 2



2/4

Figure 3

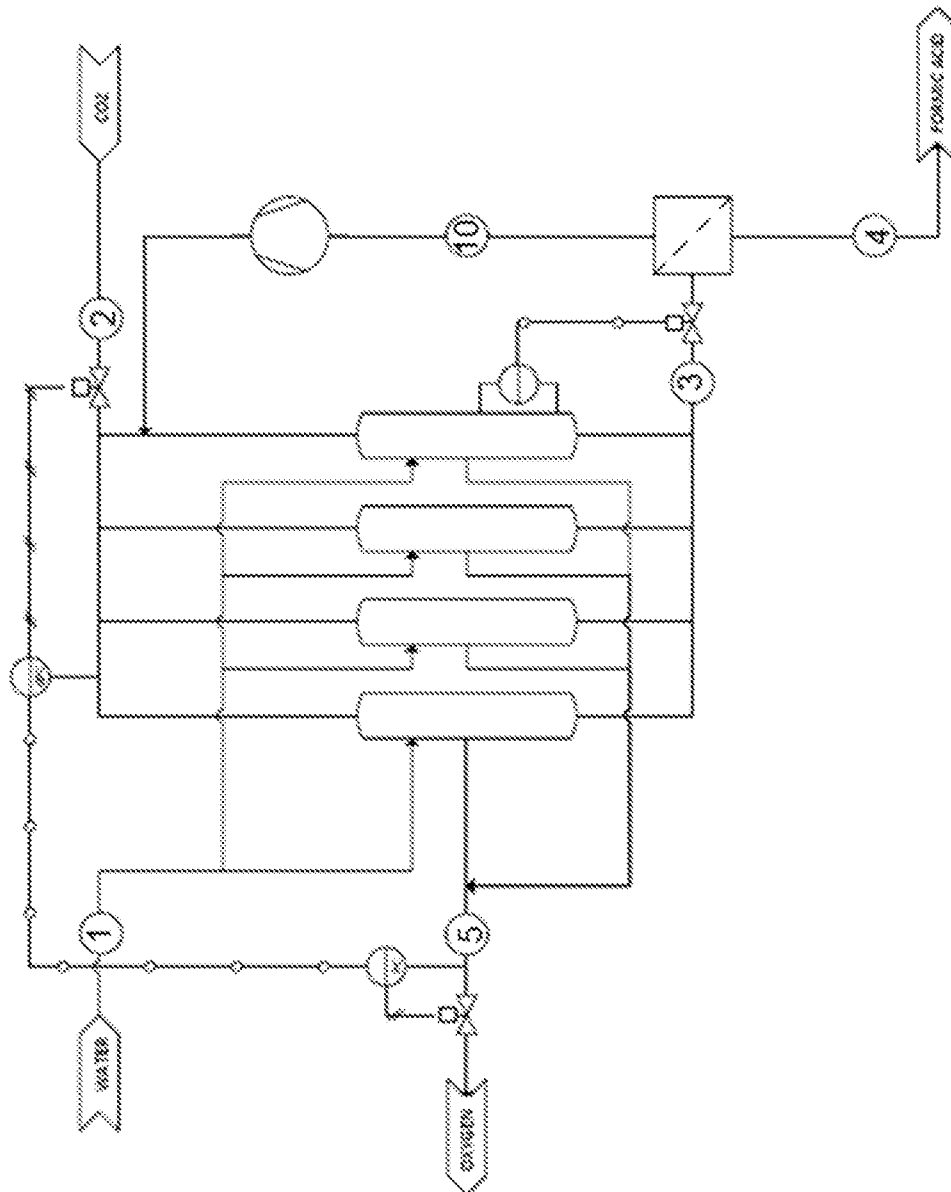
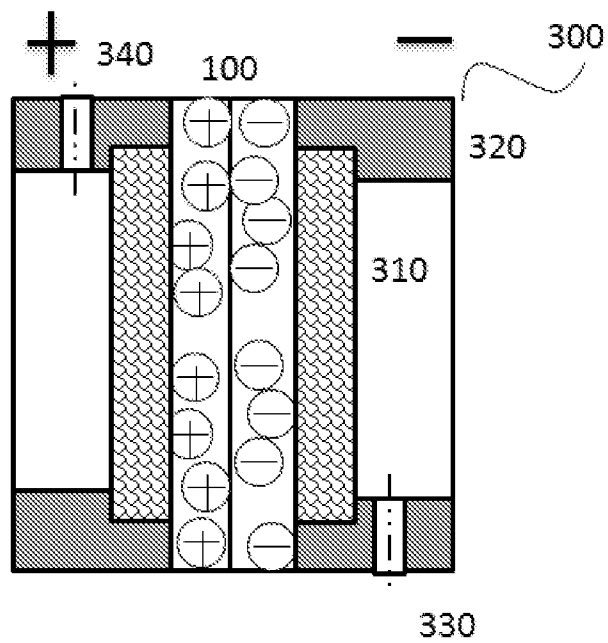


Figure 4

(A)



(B)

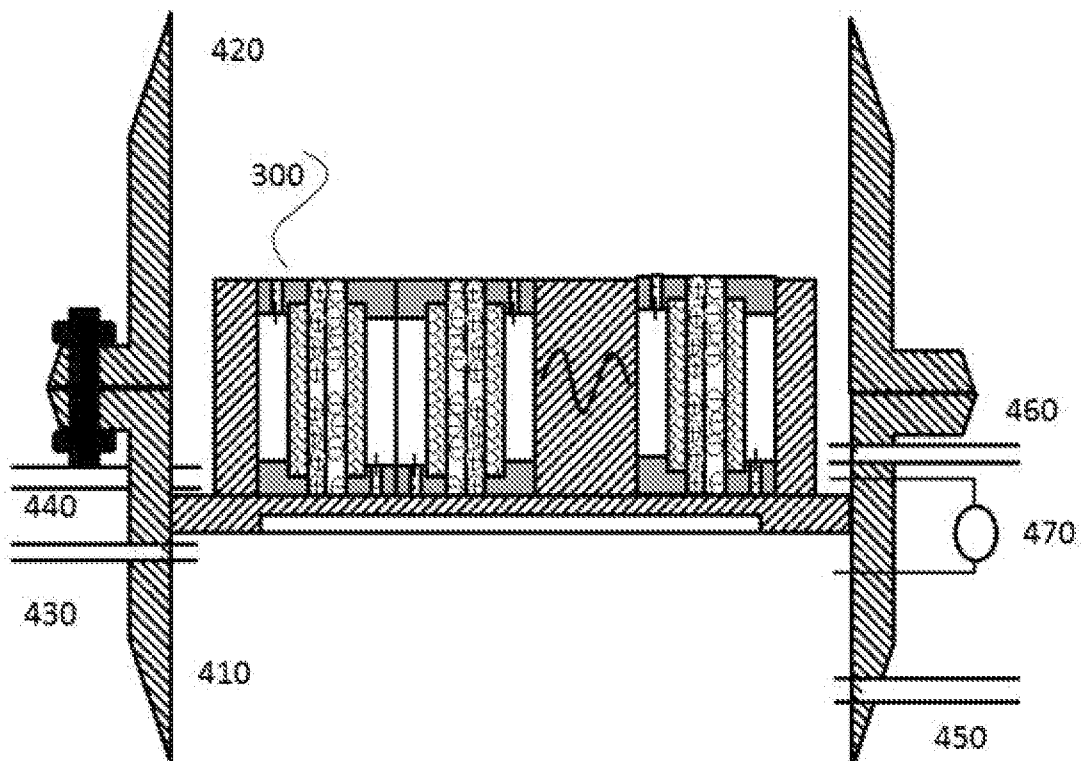
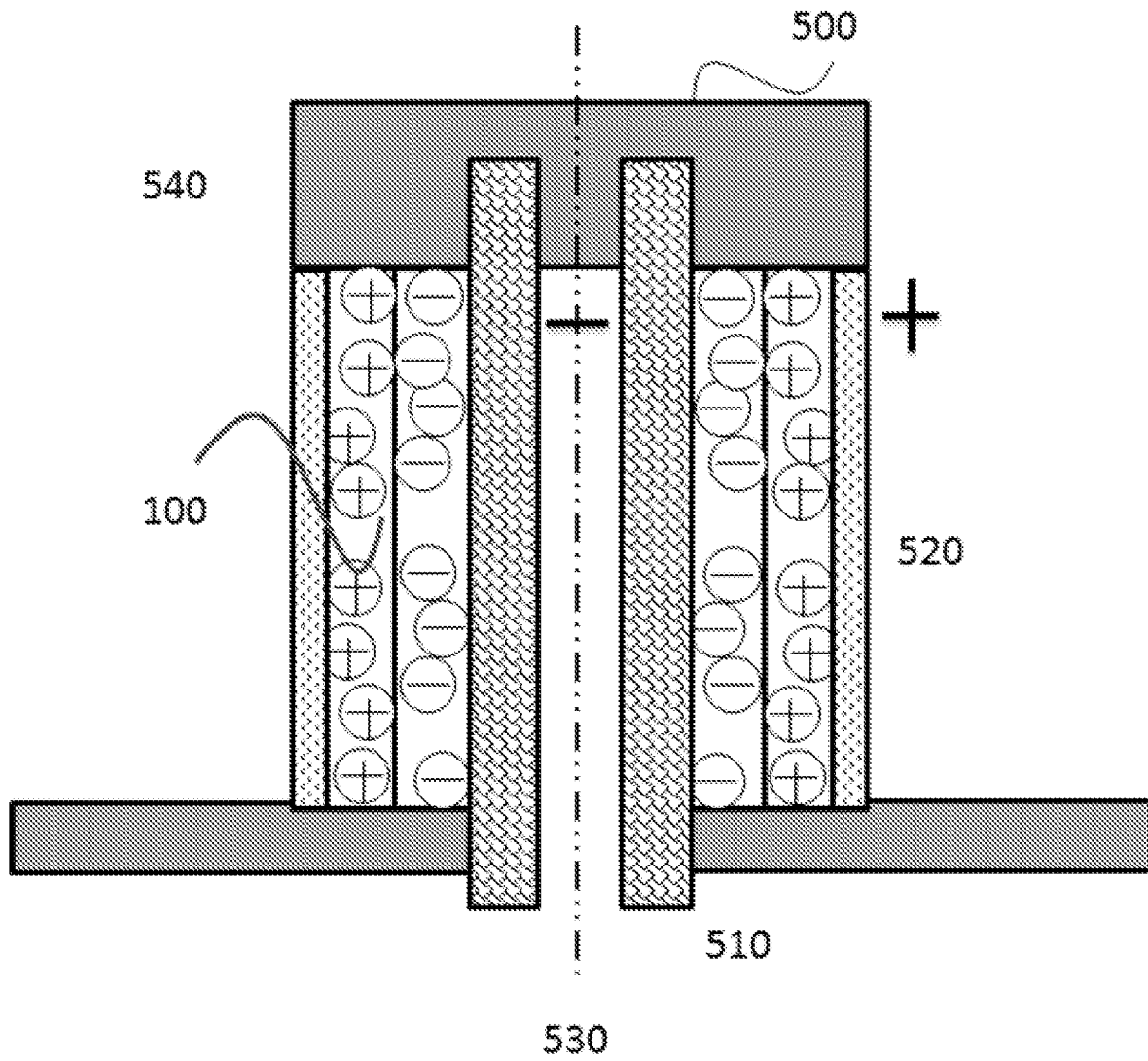


Figure 5



INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2016/050545

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25B3/04 C25B9/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C25B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	----- WO 2014/043651 A2 (LIQUID LIGHT INC [US]) 20 March 2014 (2014-03-20) paragraph [0010] - paragraph [0037]; figure 1A	1-29
Y	----- US 2013/105304 A1 (KACZUR JERRY J [US] ET AL) 2 May 2013 (2013-05-02) paragraphs [0039], [0040], [0084], [0088]; claims 1,2,10-12,16	1-29
A	----- US 2014/038019 A1 (FAN QINBAI [US]) 6 February 2014 (2014-02-06) paragraph [0006] - paragraph [0008] ----- -/-	1,24



Further documents are listed in the continuation of Box C.



See patent family annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

18 October 2016

Date of mailing of the international search report

26/10/2016

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INTERNATIONAL SEARCH REPORT

International application No

PCT/NL2016/050545

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2013/186771 A1 (ZHAI YUMEI [US] ET AL) 25 July 2013 (2013-07-25) paragraph [0055] - paragraph [0062]; claim 139; figure 1 paragraph [0077] -----	1-29

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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