

AN ELECTROCHEMICAL REACTOR SYSTEM COMPRISING STACKABLE
REACTION VESSELS

Cross-Reference to Related Application

5 [0001] This application claims the benefit of priority of Singapore Patent Application No. 10201810556T, filed 26 November 2018, the content of it being hereby incorporated by reference in its entirety for all purposes.

Technical Field

10 [0002] The present disclosure relates to an electrochemical reactor system comprising one or more stackable reaction vessels.

Background

[0003] Conventionally, batch reactors have been used for processing electrochemical
15 reactions. One example may be the reduction of CO₂ to produce various chemicals. Such batch reactors tend to suffer from static electrolyte, require large volume, poor mass transport, small active area, and/or poor separation efficiency. For instance, the static electrolyte may give rise to poor flow in the batch reactor resulting in poor mixing of reactants, the large volume may be needed to produce higher amount of products.
20 The mass transport may be limited by how fast a reactant is delivered to a catalyst's surface in a batch reactor (especially for a batch reactor with poor mixing), the small active area (e.g. of a catalyst) leads to lower turnover (i.e. poor product yield), and the poor separation efficiency may occur as batch reactors tend to be unsuitable for separating a mixture of products containing entirely gases or entirely liquids that are
25 not easily separable.

[0004] As mentioned above, conventional CO₂ reduction may be processed in batches of reaction using batch reactors. A conventional electrolytic cell, which is one example of a batch reactor, may have two compartments separated by a membrane disposed in an aqueous electrolyte. The products may typically be sequestered for chemical analysis
30 and quantification. In some instances, a single type of catalyst may be used during the entire reaction. In other instances, two or more different materials may be used as the catalyst, i.e. a "catalyst system". However, not all reactions may be carried out in the

presence of various catalytic materials, wherein the mixing of various catalytic materials to form the “catalyst system” does not address the limitations of batch reactors mentioned above, and use of such “catalyst system” does not constitute cascading chemical reactions in batch reactors (e.g. product A is first produced from the first reaction which then leads to reaction B to produce product B).

[0005] Existing micro reactors (or reactors designed in the form of micro-channels) for electrocatalytic or electrosynthesis reaction (e.g. CO₂ electrolyzers) may have serpentine turns, wherein the anode and cathode are segregated by a liquid channel flow or moistened gas flow. Such micro reactors, however, are better suited for receiving gaseous CO₂ and producing low C1 molecules like CO or formic acid (HCO₂H), which are less valuable than oxygenates and hydrocarbons containing 2 or more carbons. In the electrosynthesis type of reactors, two or more reactants may be introduced at the inlet, and the length of the serpentine micro reactors may be adjusted according to the target product molecule and the desired yield. That said, as solubility of CO₂ in aqueous solution tends to be very low and majority of the dissolved CO₂ tend to be consumed in the first 20 mm of the micro reactor even when operating at a moderate current density of about 20 mA cm⁻², the micro-channels may be restricted to liquids only and be of limited use. Bubble nucleation, e.g. from dissolved CO₂ and/or the gaseous product, may cause blockage in such micro-channels, adversely creating immense back pressure and electrolyte backflow.

[0006] Different types of micro reactors have been developed to improve the CO₂ reactant concentration. One example is to incorporate a separate gas and liquid pathway using a gas diffusion electrode. In such design, the CO₂ may be continually diffused into the electrolyte stream through a gas diffusion electrode membrane. Gas diffusion electrode and related designs involving a membrane electrode assembly, unfortunately, tend to be susceptible to high resistivity and thus poor energy conversion efficiency arising from mixtures of non-conductive polymeric membrane used. Catalyst flooding (resulting in leakage of electrolyte into gas channel) and gas leakage into electrolyte channel may also be persistent issues that need to be addressed.

[0007] In a different design incorporating a liquid “buffer layer” between proton exchange membrane and cathodic catalyst layer, the buffer layer was proposed to form an electrical double layer around the cathodic catalyst layer to lower the CO₂ conversion

cell threshold voltage. However, the resulting products are limited to lower value C1 molecules like CO or formic acid (HCO_2H).

[0008] Apart from the above, conventional flow reactors for CO_2 reduction, an example of which is shown in FIG. 1, may suffer from high current loss when the membrane resistance is increased due to increase of catalyst area. This then unfortunately requires larger voltage for the reaction to proceed and increases cost. The flow reactor of FIG. 1 may also be susceptible to gas product diffusing back into a reactant flow-in path, leakages, backflow, fluctuation, when gas-liquid crossover should not even occur in the flow reactors.

10 [0009] There is thus a need to provide for a solution that addresses one or more of the limitations mentioned above. The solution should at least provide for a system operable to produce chemicals of higher value from electrochemically reacting CO_2 .

Summary

[0010] In a first aspect, there is provided for an electrochemical reactor system comprising:

15 stackable reaction vessels, wherein each of the stackable reaction vessels is fillable with an electrolyte and comprises an anode (100), a cathode (102) and an ion selective membrane (106) arranged between the anode (100) and the cathode (102); and
 at least one gas sparger disposed across two of the stackable reaction vessels, wherein the two stackable reaction vessels are configured as an upstream stackable reaction vessel and a downstream stackable reaction vessel arranged adjacent to the upstream stackable reaction vessel, wherein the at least one gas sparger comprises (i) a pipe (202) disposed across the two stackable reaction vessels and (ii) a chamber (204) disposed in the downstream stackable reaction vessel, wherein the chamber (204) has an opening and a closed end disposed away from the opening, wherein the pipe (202) extends through the opening toward the closed end to direct gas to form a sparger headspace (206) at the closed end within the chamber (204).

Brief Description of the Drawings

20 [0011] The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention. In the following description,

various embodiments of the present disclosure are described with reference to the following drawings, in which:

[0012] FIG. 1 shows a conventional flow reactor operably for electrochemical reduction of carbon dioxide. The meaning of each reference numerals in FIG. 1 is as follows. (1) denotes CO₂ gas input, (3) denotes the cathode gas diffusion electrode (GDE), (5) denotes a catholyte, (7) denotes anolyte, (9) denotes gas products, (11) denotes liquid products, (13) denotes O₂ gas output, (15) denotes graphite current collector, (17) denotes polytetrafluoroethylene (PTFE) filter, (19) denotes poly(methyl methacrylate) (PMMA), (21) denotes anode (GDE), (23) denotes graphite current collector, and (25) denotes nafion membrane.

[0013] FIG. 2 shows a schematic of one unit of a micro flow reactor with electrolyte-filled anode (100) and cathode (102) compartments according to embodiments described herein.

[0014] FIG. 3 is a detailed view of the purging inlet (202) and purging sparger (204) designed according to embodiments described herein.

[0015] FIG. 4 is a schematic of the present electrochemical reactor system constructed from a plurality of stacked micro flow reactors, each reactors having electrolyte-filled anode (100) and cathode (102) compartments. “n” represents an integer that may range from 1 to 100 but the number of micro flow reactors is not limited to this range and may be more than 100.

[0016] FIG. 5 shows a unit of a micro flow reactor having a separate electrolyte (104) flow channel to the anode according to various embodiments described herein.

[0017] FIG. 6 shows a plurality of the stacked micro flow reactors of FIG. 5. “n” represents an integer that may range from 1 to 100 but the number of micro flow reactors is not limited to this range and may be more than 100.

Detailed Description

[0018] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised.

[0019] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments.

Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0020] The present disclosure relates to an electrochemical reactor system comprising one or more stackable reaction vessels. Each of these stackable reaction vessels may be referred to herein as a stackable micro flow reactor or a micro flow reactor. The term “stackable” used herein means that each reaction vessel may be placed adjacent to each other such that each reaction vessel is contiguous (in physical contact) with each other. The gaseous contents in a stackable micro flow reactor may be transmitted to an adjacent and contiguous stackable micro flow reactor via a pipe, tubing, manifold, etc. A single reaction vessel is shown in FIG. 2 and the stacked reaction vessels are shown in FIG. 4. The reaction vessels stacked is an arrangement where the gaseous contents (e.g. reactants, products) may flow from one reaction vessel into another without compromising the chemical reaction in each reaction vessel, as two adjacent reaction vessels may be separated by a liquid-proof but gas permeable membrane. In other words, even when the reaction vessels are in fluid communication with each other, different reactors vessels can be operated for different reactions and/or under different conditions. For example, the first reaction vessel, which is the most upstream reaction vessel, may receive reactants from a gas feed tank (114) and/or an electrolyte feed tank (116). The first reaction vessel may then be operated under a first set of conditions (e.g. pH, temperature, concentration) to produce the first product(s). One or more of the products may be channeled from the first reaction vessel into a product tank. One or more of the first products may be channeled downstream into the next reaction vessel stacked adjacent and contiguous to the first upstream reaction vessel. The next reaction vessel, which is the second reaction vessel in the stacked, may operate under a different set of conditions for a different reaction to produce one or more different products (i.e. the second products). One or more of the second products may be channeled from the second reaction vessel into a product tank. One or more of the second products may be channeled from the second reaction vessel into the next (third) reaction vessel arranged adjacent and contiguous to, and downstream of, the second reaction vessel. The third

reaction vessel may be operated under a different set of conditions from the first and/or second reaction vessels for a different reaction to produce different products. This configuration can be applied with multiple reaction vessels and not limited by the number of reaction vessels. Advantageously, the present reactor system, having such configuration, can be utilized to produce different products from a single stack of reaction vessels that are in fluid communication. As such, the present reactor system constitutes a continuous flow system and not a batch system.

[0021] Each of the reaction vessel may be configured as an electrochemical cell for processing electrochemical reactions. The reaction vessel may comprise an anode (100), a cathode (102), and an ion selective membrane (106) arranged between the anode (100) and the cathode (102). As such, each reaction vessel may be operable as an electrochemical cell. Advantageously, by stacking various electrochemical cell as described above, each cell can be operated using a smaller current source which renders the present reactor system cheaper and more efficient compared to an industrial large-sized electrochemical reactor that has been scaled up and consumes more power just to operate for a single electrochemical reaction to produce one product. As each cell is smaller, there is also lower resistance from the smaller anode (100), cathode (102) and ion selective membrane (106) used. Less electrolyte is consumed and the product turnover per unit area of the reaction vessel improves.

[0022] Details of various embodiments of the present reactor system and advantages associated with the various embodiments are now described below.

[0023] In the present disclosure, there is provided for an electrochemical reactor system comprising stackable reaction vessels. In various instances, the electrochemical reactor system may comprise one or more stackable reaction vessels. In some instances, the electrochemical reactor may comprise a plurality of the stackable reaction vessels.

[0024] Each of the stackable reaction vessels may be a micro reactor. That is to say, each reaction vessel may have dimensions in the centimetre scale. In one example, there may be ten stacked reaction vessels totaling to a height of about a meter.

[0025] The stackable reaction vessel may be arranged in various configurations. For example, the “stacking” may be vertical or lateral. Said differently, the stackable reaction vessels may be vertically stacked. The stackable reaction vessels may also be horizontally stacked. The stackable reaction vessels may be vertically and horizontally

stacked. In various instances, the stackable reaction vessels may be contiguously stacked, which means the stackable reactions vessels may be placed adjacent to and in contact with one another. The stackable reaction vessels may be in fluid communication with each other, such that the desired gas and/or liquid contents may be channeled from an upstream reaction vessel into a downstream reaction vessel. Hence, the present reactor system is versatile in its layout.

[0026] In various embodiments, each of the stackable reaction vessels may be fillable with an electrolyte (104) and may comprise an anode (100), a cathode (102) and an ion selective membrane (106) arranged between the anode (100) and the cathode (102). Each of the stackable reaction vessels may constitute an electrochemical cell. The electrolyte (104) may be a liquid, a semi-solid, or solid electrolyte. The electrolyte (104) may be a medium that provides for conduction of ions, which is to say, the electrolyte may be an ionic conductor. A semi-solid electrolyte may be, for example, a gel electrolyte. A liquid electrolyte may be an aqueous electrolyte. The reaction vessel may be filled with a liquid electrolyte that converts into a solid form, and hence the liquid electrolyte may operate as a solid electrolyte. In other instances, the reaction vessel may be filled with a solid electrolyte by having the solid electrolyte constructed therein. Non-limiting examples of a solid electrolyte may include ceramics and solid polymers. The electrolyte (104) may also be a liquid medium mixed with such solids to render the electrolyte (104) ion-conducting. The anode (100) and cathode (102) may be in contact directly with the electrolyte (104).

[0027] The electrochemical reactor system may comprise at least one gas sparger disposed across two of the stackable reaction vessels, wherein the two stackable reaction vessels may be configured as an upstream stackable reaction vessel and a downstream stackable reaction vessel arranged adjacent to the upstream stackable reaction vessel. The term “gas sparger” used herein refers to a component in the reaction vessel used to distribute reactant gases into the electrolyte.

[0028] The at least one gas sparger may comprise (i) a pipe (202) disposed across the two stackable reaction vessels and (ii) a chamber (204) disposed in the downstream stackable reaction vessel. The chamber (204) may have an opening and a closed end disposed away from the opening. The pipe (202) may extend through the opening toward the closed end to direct gas to form a sparger headspace (206) at the closed end

within the chamber (204). In other words, the pipe (202) may have one end that serves as the inlet for gases from an upstream reaction vessel to flow into a downstream reaction vessel arranged adjacent and contiguous to the upstream reactor. Such a pipe (202) may be referred to herein as a “purging inlet”. The gaseous product generated in the upstream reactor vessel may be channeled into the adjacent downstream reactor vessel through the pipe (202) of the gas sparger and into the chamber (204) of the gas sparger, wherein the chamber (204) is disposed in the downstream reaction vessel. As the chamber (204) is the component for purging/distributing gases into the reaction vessel, the chamber (204) may be termed herein as “purging sparger”. The pipe (202) and the chamber (204) configured in this manner forms a headspace (206) in the gas sparger. As this headspace (206) is formed in the chamber (204) of the gas sparger, it may be termed herein as a “sparger headspace” or “purging headspace”.

[0029] The gas products directed from an upstream reaction vessel to the closed end of the chamber (204) accumulates thereat, forming the sparger headspace (206). Advantageously, the inverted (upside down) configuration of the chamber (204) having the sparger headspace (206) not only provides for more efficient diffusion of gaseous reactant(s), but also at the same time prevents flow of an electrolyte from the downstream reaction vessel to the upstream reaction vessel.

[0030] In various embodiments, the pipe (202) and the opening of the chamber (204) may be arranged to allow the gas to flow from the upstream stackable reaction vessel through the pipe (202) into the adjacent downstream stackable reaction vessel which the chamber (204) may be disposed in, and to prevent the electrolyte from flowing through the pipe (202) in a direction opposite to the flow of the gas. Such an arrangement also prevents backflow of an electrolyte in the downstream reaction vessel back into the upstream vessel. Such an arrangement may include having the inlet of the pipe (202) disposed proximal to the closed end of the chamber (204) and/or away from the opening of the chamber (204).

[0031] Each of the stackable reaction vessels may be designed to have a reaction headspace formable therein. The reaction headspace is to be distinguished from the purging headspace in that the reaction headspace is disposed in the reaction vessel but outside the chamber (204) of the gas sparger while the purging headspace (206) is in the chamber (204). The reaction headspace separates and accumulates the gaseous

phase (either reactant feed or reaction product) from the electrolyte (104) (may be solid, liquid or semi-solid form), so as to minimize electrolyte (104) transfer to subsequent downstream vessels. Said differently, the reaction headspace advantageously allows for separation of gases (gaseous feedstock and/or reactant products) from the electrolyte (104) (may be solid, liquid or semi-solid) in a reaction vessel. If there is no reaction headspace, the electrolyte (104) may flow into downstream reaction vessels, causing leakage or flooding issues. Bubble nucleation and related back pressure issues, as already mentioned above, may also occur.

[0032] Additionally, the reaction headspace prevents the electrolyte (104) from flowing through the pipe (202) from the downstream stackable reaction vessel to the upstream stackable reaction vessel arranged adjacent to the downstream stackable reaction vessel. The reaction headspace may be formed and/or maintained by the filling of the electrolyte (104) and pressure in the one or more reaction vessels.

[0033] The various arrangements of the pipe (202) and chamber (204) discussed above, which shall not be iterated for brevity, may include an arrangement where the opening of the chamber (204) faces a direction opposite to which the gas flows through the pipe (202) from the upstream stackable reaction vessel into the adjacent downstream stackable reaction vessel.

[0034] In the present electrochemical reactor system, a liquid-proof gas permeable membrane may be arranged between the upstream stackable reaction vessel and the adjacent downstream stackable reaction vessel to prevent liquid and the electrolyte (104) migrating between the upstream stackable reaction vessel and the adjacent downstream stackable reaction vessel. In other words, the liquid-proof gas permeable membrane prevents mixing of the liquid and the electrolyte (104) contents that are in one reaction vessel with another even when the reaction vessels are arranged contiguous to each other and in fluid communication. The liquid may be a reaction product or may contain a reaction product. The liquid-proof gas permeable membrane, however, allows for gaseous products of an upstream reaction vessel to flow to a downstream reaction vessel that is arranged adjacent and contiguous to the upstream reaction vessel. The liquid-proof gas permeable membrane may be, for example, a water-proof gas permeable membrane. The liquid-proof gas permeable membrane may be made of a fluoropolymer, which may deform and/or rupture easily depending on thickness of the

liquid-proof gas permeable membrane. The liquid-proof gas permeable membrane may be arranged on a support (108) to enhance mechanical strength of the liquid-proof gas permeable membrane. The support (108) may be in the form of a mesh, woven fibers, or a porous solid, that allows gas to diffuse through and yet has sufficient mechanical strength to reinforce the liquid-proof gas permeable membrane. A non-limiting example of materials for the support (108) may include polyamide (e.g. nylon or Kevlar). The support (108) may be a non-metallic material as metals may contaminate the reaction and the reaction vessel.

[0035] As already mentioned above, each of the reaction vessel may comprise an anode (100) and a cathode (102). Either or both of the anode (100) and the cathode (102) may comprise a catalyst configured to perform an electrochemical reaction in each of the stackable reaction vessels. The electrochemical reaction operable in each of the stackable reaction vessels may be different, which means that the catalyst used in each of the reaction vessels need not be the same. With this, the present electrochemical reactor system is advantageously operable for cascading electrochemical reactions, for example, wherein a series of electrochemical reactions can be carried out at the same time. Additionally, the present electrochemical reactor system circumvents the constraint faced by a conventional large-sized industrial reactor tank where specific catalyst(s) has to be used. To elaborate, if the industrial reactor tank has to processed different reactions requiring different catalysts, then separate reactor tanks have to be built, thus occupying more land space. Alternatively, the industrial reactor tank has to be undesirably operated as a batch reactor and not a continuous reactor.

[0036] Each of the stackable reaction vessels may comprise an anode compartment and a cathode compartment which the anode (100) and the cathode (102) in each of the stackable reaction vessels are coupled to, respectively. For example, the compartment in which the anode (100) may be disposed in, is termed the anode compartment, and the compartment in which the cathode (102) may be disposed in, is termed the cathode compartment. The term "coupled" used herein means the anode (100) and the cathode (102) are electrically connected to their respective compartments such that the reaction vessel can be operated to perform an electrochemical reaction. For example, the anode (100) need not be disposed in the center of the anode compartment within the reaction

vessel, instead, the anode (100) may be deposited on or formed as one or more of the walls defining the anode compartment. This may apply for the cathode (102).

[0037] The anode compartment may be formed in each of the stackable reaction vessels. In certain embodiments, the anode compartment may be shaped to have a serpentine flow channel (500). A serpentine flow channel (500) may be used to improve anodic oxidation reaction kinetics of a reaction vessel and/or accommodate alternative reactions that can take place at the anodic (oxidation) compartment. For example, water oxidation to oxygen or organic contamination oxidation (decontamination) may be performed by supplying a separate anodic electrolyte (anolyte) through a second electrolyte tank (506). In such instances, the anode compartment may be in fluid communication with a second electrolyte tank (506).

[0038] The cathode compartment may be formed in each of the stackable reaction vessels, and wherein the cathode compartment may be in fluid communication with a first electrolyte tank (116). The first electrolyte tank (116) may be used for introducing liquid reactants (e.g. electrolyte) to or storing extracted liquid products (e.g. recycling of electrolyte) from one or more reaction vessels.

[0039] In the present electrochemical reactor system, two of the stackable reaction vessels may each comprise the cathode compartment being in fluid communication with a gas tank (114). The gas tank (114) may be used for introducing gaseous reactants to or storing extracted gas products from one or more reaction vessels.

[0040] Based on the above, the present electrochemical reactor system is additionally versatile in that each reaction vessel can be connected to one or more electrolyte and/or gas tanks (114, 116, 506) for introducing reactants to or storing extracted products from.

[0041] In certain embodiments, the anode compartment may be an opened compartment exposed to atmosphere. In other words, the anode compartment may be exposed to air. In other instances, the anode compartment may be a closed compartment to avoid direct exposure or entirely eliminate exposure to air.

[0042] In the present electrochemical reactor system, the anode (100) and the cathode (102) each may have (i) a length ranging from 0.5 cm to 3 cm, 0.5 cm to 2.5 cm, 0.5 cm to 2 cm, 0.5 cm to 1.5 cm, 0.5 cm to 1 cm, 1 cm to 3 cm, 1.5 cm to 3 cm, 2 cm to 3 cm, 2.5 cm to 3 cm, 1 cm to 2 cm, 1.5 cm to 2 cm, and/or (ii) a diameter ranging from 0.5 to 3 cm, 0.5 cm to 2.5 cm, 0.5 cm to 2 cm, 0.5 cm to 1.5 cm, 0.5 cm to 1 cm, 1 cm

to 3 cm, 1.5 cm to 3 cm, 2 cm to 3 cm, 2.5 cm to 3 cm, 1 cm to 2 cm, 1.5 cm to 2 cm. The anode (100) and the cathode (102) may have a rectangular shape (cuboid) with a length as mentioned above. The anode (100) and the cathode (102) may be tubular having a diameter as mentioned above. Such dimensions are already advantageous over industrial reactors that have to utilize large anode and cathode. Such dimensions help to maintain a smaller net usage of currents to operate the stacked reaction vessels, which translates into cheaper and low-end current-voltage sources used.

[0043] In the present electrochemical reactor system, the anode (100) and the cathode (102) in each of the stackable reaction vessels may be spaced apart at 2 cm or less, 1 cm to 2 cm, or at 1 cm or less. This advantageously reduces ohmic loss and still allows efficient mass transport of reactants and products in the reaction vessels.

[0044] In various embodiments, the chamber (204) may be constructed of a plastic comprising polyether ether ketone or polyetherimide.

[0045] In various embodiments, each of the stackable reaction vessels may be constructed from a chemically inert material comprising a fluorinated polymer. As non-limiting examples, the fluorinated polymer may comprise polytetrafluoroethylene, ethylenetetrafluoroethylene, polychlorotrifluoroethylene. In various embodiments, each of the stackable reaction vessels may be constructed from a chemically inert material comprising polytetrafluoroethylene, ethylenetetrafluoroethylene, polychlorotrifluoroethylene, or polyether ether ketone.

[0046] The present reactor system is able to operate in a manner where each reaction vessel is run at conditions of about room temperature and pressure to lower the energy requirement, which renders it unlikely for undesirable high vapour pressure to occur. Nevertheless, the present electrochemical reactor system may further comprise a gas permeable membrane disposed at an end of the pipe (202) proximal to the closed end of the chamber. This advantageously reduces vapor cross-over (flowing back) from a downstream reaction vessel into an upstream reaction vessel. While a reaction vessel may be operated at room temperature and pressure, having the gas permeable membrane mitigates and/or prevents the vapour cross-over when the reaction conditions in a reaction vessel increase to or require higher pressure and temperature that in turn increases vapour pressure of an electrolyte (104), especially for solid and/or semi-solid electrolytes (104). Different electrolyte solutions and/or non-aqueous

solvents with much lower equilibrium vapour pressure (e.g. ionic liquids or acetonitrile) may be used in the present electrochemical reactor.

[0047] In addition, the present electrochemical reactor system is compatible with dehumidifiers and/or scrubbers, which may be incorporated to an outlet of one or more of reaction vessels, prior to separation of the gas and/or liquid product(s). A wide range of technologies that allows liquid (e.g. water) removal from air (e.g. refrigeration, deliquescence, desiccant or membrane) may be incorporated without affecting the extraction of the gas and/or liquid product(s). The gas permeable membrane, the use of electrolyte solutions and/or non-aqueous solvents having lower equilibrium vapour pressure, the dehumidifiers and/or scrubbers and incorporation of technologies that allows liquid removal from air and gaseous products, help to mitigate high vapour pressure in the stacked reaction vessels, and dry up the gas before the gas finishes travelling through the stack reactions vessels from the first reaction vessel to the last reaction vessel. Hence, the present reactor system may be used even if the reactions require, for example, higher pressure and temperature to enhance reaction kinetics and conversion rate.

[0048] The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

[0049] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0050] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance.

[0051] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

[0052] Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

Examples

[0053] The present disclosure relates to an electrochemical reactor system comprising a plurality of stackable reaction vessels. Said differently, a stackable electrochemical reactor system is described herein. The stackable electrochemical reactor system may be referred to herein as micro flow reactor system. The micro flow reactor system may be operable for electrochemical conversion reactions.

[0054] The present micro flow reactor system is advantageous as it separates the gas diffusion and electrode function, which reduces complications in electrolyte/gas leakage. The reactor stack incorporates the benefits of having a flow system. At the same time, including a headspace allows the electrolytic reaction to occur in the aqueous phase while providing a purging sparger (204) to allow intermixing between gaseous feedstock and liquid electrolyte. The purging sparger also effectively prevents electrolyte backflow and flooding, which is a problem in conventional continuous flow reactors.

[0055] Cascading reaction design for processing different reactions requiring different catalysts and conditions is also achievable, as the present system allows for incorporation of different catalytic system and processing under different reaction conditions to obtain a particular chemical product of interest or different products.

[0056] The present electrochemical reactor system is described in further details, by way of non-limiting examples, as set forth below.

[0057] Example 1: Materials for Construction and General Configuration of the Present Electrochemical Reactor System

[0058] The present micro flow electrochemical reactor system consists of stackable, smaller (micro) flow reactors connected together through a water-proof but gas permeable membrane, forming a cascade of micro flow reactors. Each micro flow reactor has two compartments for the anode (100) and cathode (102), separated by an ion selective membrane (104) that prevents product crossover and dilution from cathode compartment to anode compartment, or vice versa (see FIG. 2). Each of the micro flow reactors may be referred to herein as a reaction vessel.

[0059] The present reactor system is designed such that at least one gas sparger is disposed across two of the stackable reaction vessels. The at least one gas sparger has a pipe (202) and a chamber (204). In particular, the micro flow reactor has a “purging

inlet”, which is a pipe (202) that extends into a downstream reaction vessel from an upstream adjacent vessel such that the pipe (202) is disposed in two contiguous reaction vessels. The chamber (204), also referred to herein as a “purging sparger”, is disposed only in the downstream reaction vessel of two contiguous reaction vessel which the gas sparger extends across (see FIG. 3). The chamber (204), in this instance as a non-limiting example, is positioned as an inverted (i.e. upside down) container that can be submerged in an electrolyte filled in the reaction vessel. This configuration allows for a headspace (206) to form as gas entering the chamber (204) through the pipe (202) is directed to the closed end of the chamber to form the headspace (206) in the chamber (204). This headspace may be termed herein as a “purging headspace” or a “sparger headspace”.

[0060] Advantageously, the sparger headspace (206) prevents liquid crossover into the pipe (202) and backflow to upstream reaction vessel. Apart from the gas sparger shown in FIG. 3, other gas sparger design, such as a commercially available sparger, micro sparger, or gas diffusion membrane, may be used as long as it provides for such advantage. The micro flow reactors can be connected to a gas tank (114) and a liquid tank (116) for the purpose of sampling, concentrating, separating, including accumulating gaseous and liquid products, respectively. The liquid tank (116) can be an electrolyte tank (116) (i.e. store and/or supply electrolyte). The gas and liquid reactants or products may be circulated through or recycled through such gas tank (114) and liquid tank (116).

[0061] Different types of catalysts (in the anode (100) and cathode (102) in FIG. 2) can be incorporated to the micro flow reactors to increase the rate and selectivity of the electrochemical reactions involved. The micro flow reactors with different types of catalyst are combined or stacked together to form a micro flow reactor stack capable of performing cascading chemical reactions. FIG. 4 depicts an example of “n” numbers of micro flow reactors stacked vertically. “n” may be an integer from 1 to 100, or even more than 100.

[0062] For construction of each reaction vessel, the materials of choice include, but are not limited to, fluorinated polymers such as polytetrafluoroethylene (PTFE), ethylene tetrafluoroethylene (ETFE), or polychlorotrifluoroethylene (PCTFE), for their chemical

inertness. For the same advantage, polyether ether ketone (PEEK) is also a suitable material.

[0063] For such stackable reaction vessels, smaller anode (100) and cathode (102) sizes are preferred. The dimensions can range from 0.5 cm to 3 cm (in terms of length for rectangular shape and/or diameter for circular shape) to keep the net operating current per reaction vessel small for cheaper, low-end current/voltage source to be used, which can be under 1 A of raw current per cell as an example. To reduce ohmic loss, shorter distance between anode (100) and cathode (102) can be arranged but still allowing for efficient reactant mass transport. The distance can be 1 cm to 2 cm or smaller.

10 **[0064] Example 2: Arrangement of Purging Inlet and Purging Sparger**

[0065] The present reactor system incorporates headspace and purging sparger (204) that is connected from a downstream reactor as already mentioned above and illustrated through FIG. 2 and FIG. 3. Harder and stiffer plastic can be used for the construct of the gas sparger, which include but is not limited to PEEK and polyetherimide. The purging sparger (204) can have a small diameter, e.g. 1/8 inch (about 0.32 cm) or smaller, but other dimensions can be accommodated. The purging sparger (204) is also configured to have an upside down cap design (FIG. 3), which directs gaseous flow from upstream reactors to the electrolyte (104) of the downstream reactor and prevents backflow of the electrolyte (104). An additional flow check valve may be incorporated to the purging inlet (i.e. pipe (202)) to reinforce backflow protection.

20 [0066] Backflow and electrode flooding is a problematic issue in gas diffusion type of reactor, both of which are addressed by the present reactor system. The present reactor system, which allows for a headspace (not the headspace (206) in the chamber (204) of the gas sparger) in each of the reaction vessels, advantageously renders for production of higher value products having two or more carbons, also known herein as C2+ molecules.

25 **[0067] Example 3: Cascade Arrangement of Reaction Vessels**

[0068] The present reactor system advantageously allows for a cascading reaction design. In the present reactor system, different catalytic system (catalyst and electrolyte (104)) can be incorporated to each of the reaction vessels stacked as shown in FIG. 4, such that different reaction environments (e.g. temperature, stirring) can be operated to increase the rate and selectivity of the electrochemical reactions in each of the reaction

vessels. In other words, the present reactor system allows a “mix-and-match” operation of different reactions requiring different conditions in a “single reactor stack”. The micro flow reactors having different types of catalyst are combinable or stacked together, forming a group of micro flow reactors capable of performing cascading chemical reactions. FIG. 4 depicts an example of “n” numbers of micro flow reactors stacked vertically, wherein n can be an integer from 1 to 100 and not limited to 100.

[0069] A serpentine flow-channel configuration, as a non-limiting example, can be used for the compartment which the anode (100) is incorporated to, so as to improve the anodic oxidation reaction kinetics of the micro flow reactors (FIG. 5). The serpentine flow-channel adds the possibility of accommodating alternative reactions on the anodic (oxidation) side. For example, water oxidation to oxygen or organic contamination oxidation (decontamination) can be performed by supplying a separate anodic electrolyte in the liquid (i.e. electrolyte) tank (506).

[0070] FIG. 6 depicts, as an example, “n” numbers of micro flow reactors with serpentine flow channel configuration stacked vertically.

[0071] **Example 4: Summary of Present Electrochemical Reactor System**

[0072] The present reactor system comprises stackable micro flow reactors for electrochemical conversion reactions, advantageously allowing for different catalysts to be incorporated to each of the reaction vessels. This enables the stacked reaction vessels to be operated for cascading (electro)chemical reactions, resulting in a more targeted reaction for more specific and higher value products. In general, the higher value products are, for example, hydrocarbons and oxygenates with two or more carbons, also known herein as C2+ molecules.

[0073] In an electrochemical reactor, specifically in the case of CO₂ reduction, the present micro flow reactors allow continuous replenishment of CO₂ without the need for a gas diffusion electrode (GDE). The products and unreacted CO₂ can be funnelled to subsequent micro flow reactors to increase the overall CO₂ conversion. A significant advantage of this is that cascading reactions can be facilitated by introducing a series of different catalyst types, electrolyte types and reaction environments in the compartment, which the cathode (102) is incorporated to, of downstream reaction vessels to form C2+ products. An example of this is illustrated in FIG. 4 and/or FIG. 6.

[0074] At the most upstream reaction vessel (marked “A” in FIG. 4 and 6), the catalyst incorporated can convert CO₂ to C1 molecules, e.g. carbon monoxide (CO) can be produced. For this purpose, the most upstream reaction vessel A may be configured/operated as a non-aqueous electrolyte system to suppress the competitive hydrogen evolution reaction.

[0075] In the midstream reaction vessel (marked “B” in FIG. 4 and 6), the catalyst incorporated therein can, for example, convert CO₂ to C2 molecules, e.g. to produce ethylene (C₂H₄). For this purpose, the reaction vessel B can be filled with an aqueous carbonate electrolyte.

[0076] In downstream reaction vessels (marked “C” and “D” in FIG. 4 and 6), the catalysts respectively incorporated therein can, for example, facilitate hydroformylation between (C₂H₄) and CO to form C3 molecules, e.g. to produce propanol (C₃H₇OH) or propionaldehyde (C₂H₅CHO).

[0077] The above reactions demonstrated may be summarized using the chemical equations as follows:

Reaction Vessel A: CO₂ → CO

Reaction Vessel B: CO₂ → C₂H₄

Reaction Vessel C: H₂O → H₂

Reaction Vessel D: C₂H₄ + CO + H₂ → C₂H₅CHO

[0078] As demonstrated above, the present reactor system advantageously provides for cascading reactions, as the present system is able to offer flexibility in better targeting a specific product of higher economic or energy value. Different sets of electrolyte can also be accommodated in each of the reaction vessels stacked. Moreover, as different reactions require different operating conditions (e.g. pH, concentration or types of counter ions), the present reactor system advantageously allows for different reactions and multiple products to be produced within a “single reactor”. Each reaction vessel can be coupled to a circulation and/or an extraction unit or system independent of the other reaction vessel, which leads to easier product separation.

[0079] Besides, the inverted chamber (204) allows efficient diffusion of main reactant gas from, e.g. tank (114), or a secondary reactant gas from an upstream reaction vessel stacked, into the electrolyte (104) of an adjacent downstream reactor stacked while preventing the backflow of liquid.

[0080] Another flexibility of present reactor system is that the compartment which the anode (100) is coupled to or incorporated to can be a closed chamber fillable and operable with an electrolyte (104), or open to air (with a gas permeable layer incorporated for passage of air) similar to the construction of zinc-air battery. Another flexibility of this is that a secondary flow reaction can be added to the anode (100) side, e.g. for toxic waste degradation, water purification.

[0081] **Example 5: Commercial and Potential Applications**

[0082] One of the potential uses of the micro flow reactor system described herein is for the conversion of carbon dioxide to chemicals of higher value. Non-limiting examples of such higher value chemicals include ethylene, formic acid, oxalic acid, acetic acid, and propanal. The higher value chemicals can also be fuels such as ethanol, propanol, etc. Apart from CO₂, other green house gases may be converted to products of higher economic or energy value.

[0083] The present reactor system can also be used for processing other reactions, such as but not limited to, conversion of carbon monoxide and/or methane to higher value chemicals, water splitting which converts water to hydrogen and oxygen, conversion of nitrogen to ammonia, water purification, or organic contamination degradation, etc.

[0084] The present reactor system is further operable for water treatment processes and hydroformylation, and operable with or operable as a liquid and gas diffusion reactor system.

[0085] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. An electrochemical reactor system comprising:
stackable reaction vessels, wherein each of the stackable reaction vessels is fillable with an electrolyte and comprises an anode, a cathode and an ion selective membrane arranged between the anode and the cathode; and
at least one gas sparger disposed across two of the stackable reaction vessels, wherein the two stackable reaction vessels are configured as an upstream stackable reaction vessel and a downstream stackable reaction vessel arranged adjacent to the upstream stackable reaction vessel, wherein the at least one gas sparger comprises (i) a pipe disposed across the two stackable reaction vessels and (ii) a chamber disposed in the downstream stackable reaction vessel, wherein the chamber has an opening and a closed end disposed away from the opening, wherein the pipe extends through the opening toward the closed end to direct gas to form a sparger headspace at the closed end within the chamber.
2. The electrochemical reactor system of claim 1, wherein the pipe and the opening of the chamber are arranged to allow the gas to flow from the upstream stackable reaction vessel through the pipe into the adjacent downstream stackable reaction vessel which the chamber is disposed in, and to prevent the electrolyte from flowing through the pipe in a direction opposite to the flow of the gas.
3. The electrochemical reactor system of claim 1 or 2, wherein each of the stackable reaction vessels is designed to have a reaction headspace formable therein, wherein the reaction headspace prevents the electrolyte from flowing through the pipe from the downstream stackable reaction vessel to the upstream stackable reaction vessel arranged adjacent to the downstream stackable reaction vessel.
4. The electrochemical reactor system of any one of claims 1 to 3, wherein the opening of the chamber faces a direction opposite to which the gas flows through the pipe from the upstream stackable reaction vessel into the adjacent downstream stackable reaction vessel.

5. The electrochemical reactor system of any one of claims 1 to 4, wherein a liquid-proof gas permeable membrane is arranged between the upstream stackable reaction vessel and the adjacent downstream stackable reaction vessel to prevent liquid and the electrolyte migrating between the upstream stackable reaction vessel and the adjacent downstream stackable reaction vessel.
6. The electrochemical reactor system of any one of claims 1 to 5, wherein either or both of the anode and the cathode comprise a catalyst configured to perform an electrochemical reaction in each of the stackable reaction vessels, wherein the electrochemical reaction in each of the stackable reaction vessels is different.
7. The electrochemical reactor system of any one of claims 1 to 6, wherein each of the stackable reaction vessels comprises an anode compartment and a cathode compartment which the anode and the cathode in each of the stackable reaction vessels are coupled to, respectively.
8. The electrochemical reactor system of claim 7, wherein the anode compartment is formed in each of the stackable reaction vessels, and wherein the anode compartment is shaped to have a serpentine flow channel.
9. The electrochemical reactor system of claim 7 or 8, wherein the anode compartment is in fluid communication with a second electrolyte tank.
10. The electrochemical reactor system of any one of claims 7 to 9, wherein the anode compartment is an opened compartment exposed to atmosphere.
11. The electrochemical reactor system of any one of claims 7 to 10, wherein the cathode compartment is formed in each of the stackable reaction vessels, and wherein the cathode compartment is in fluid communication with a first electrolyte tank.

12. The electrochemical reactor system of any one of claims 1 to 11, wherein two of the stackable reaction vessels each comprise the cathode compartment being in fluid communication with a gas tank.
13. The electrochemical reactor system of any one of claims 1 to 12, wherein the anode and the cathode each have (i) a length ranging from 0.5 cm to 3 cm, and/or (ii) a diameter ranging from 0.5 to 3 cm.
14. The electrochemical reactor system of any one of claims 1 to 13, wherein the anode and the cathode in each of the stackable reaction vessels are spaced apart at 2 cm or less.
15. The electrochemical reactor system of any one of claims 1 to 14, wherein the chamber is constructed of a plastic comprising polyether ether ketone or polyetherimide.
16. The electrochemical reactor system of any one of claims 1 to 15, wherein each of the stackable reaction vessels is constructed from a chemically inert material comprising polytetrafluoroethylene, ethylenetetrafluoroethylene, polychlorotrifluoroethylene, or polyether ether ketone.
17. The electrochemical reactor system of any one of claims 1 to 16, further comprising a gas permeable membrane disposed at an end of the pipe proximal to the closed end of the chamber.
18. The electrochemical reactor system of any one of claims 1 to 17, wherein the stackable reaction vessels are vertically stacked.
19. The electrochemical reactor system of any one of claims 1 to 18, wherein the stackable reaction vessels are horizontally stacked.

20. The electrochemical reactor system of any one of claims 1 to 19, wherein the stackable reaction vessels are contiguously stacked.