

MEC System

The present invention relates to a Microbial Electrolysis Cell (MEC) system and in particular to a MEC system stacking multiple MECs into MEC stacks for conducting a bio-electromethanogenesis reaction.

- 5 Methane has the highest energy density per carbon atom among fossil fuels and its potential for energy conversion is far greater than any other natural gas, obtained directly by combustion in presence of oxygen or using fuel cells to produce electricity. Methane's potential for energy generation has become increasingly relevant in the global market.

- 10 Methane produced from renewable sources (renewable-methane), constitutes a sustainable and renewable energy source and already today increasingly substitutes coal and other fossil fuels. Hence many different processes for the generation of renewable-methane, so-called methanation processes are being developed and optimized in the prior art.

- 15 One methanation process can for example be based on microbial electrochemical technology (MET) referred to as bio-electromethanation. This process is realized in a microbial electrolysis cell (MEC), which is a unique system capable of converting electrical energy into chemical energy while employing microbes as catalysts. The system achieves the combination of electrolysis and methane production in one single reactor, the so called MEC. If within the MEC methanogenic microorganisms reside e.g. in the cathode compartment or at the cathode, the MEC will be regarded as bio-electromethanation cell.

- 20 The reactor may comprise a single compartment, or the cathodic compartment or chamber, which may be separated from the anodic compartment or chamber, via e.g. a semipermeable membrane. In some embodiments of the state of the art methanogenesis by the methanogenic microorganisms (e.g. methanogens or archaea) takes place directly in the bio-cathode compartment, whereby the electron flow required for the cathodic reduction of CO₂ to methane
25 is compensated in the anode compartment by water oxidation.

In more detail, within this process electrical power is used to enhance the potential difference between the anode and the cathode of MEC to enable the bio-electromethanation reaction.

The cathodic MEC process generates electrons that will be utilized as an electron-donor, e.g. in form of hydrogen to reduce a carbon source, e.g. carbon dioxide to a valuable product, e.g. methane. The involved bio-electromethanation reaction is catalysed by microorganisms the so-called bio-catalyst.

- 5 In the present invention the term “input gas” will be used and is understood to encompass any gas required by or suitable for a catalyst in the MEC to achieve a chemical reaction. Suitable input gas can be selected from typical carbon donors like CO₂ or CO, but also from waste gases containing beside others suitable carbon donors.

- According to the present invention input gases are also to be understood as CO₂ rich emissions
10 and/or waste gas that are found or produced as a side product during activities performed in industrial processes such as fossil fuel or agricultural industries of either microbial fermentation e.g. in the ethanol production, the combustion of fossil fuels e.g. in coal burning energy plants or e.g. as side product of geothermal power plants or e.g. as a result of any human industrial activity resulting in the emission of gas compositions, otherwise dispersing into the atmosphere, such as
15 cattle farming and other agricultural activities. Such gases depending on their source may comprise very different gas compositions. They have primarily in common that they contain a relatively high amount of CO₂ in comparison to air.

- According to another embodiment of the present invention instead of input gas also another inorganic carbon source comprising electron equivalents can be used and are selected from the
20 group consisting of sodium carbonate, potassium carbonate and ammonium carbonate or combinations of the aforementioned.

- To increase production of methane employing bio-electromethanation MECs are stacked into so called MEC stacks. A MEC stack consist of several MECs herein also called MEC cells. The MECs can be built up from layers. Layers are e.g. membranes, electrodes, sealing, (porous) transport layers,
25 turbulence promoters, electrode-membrane assemblies, and bipolar plates. This design allows for simplified expandability of the MECs and also easy replacement of individual or broken MEC, if needed. Thus, this design allows simplified maintenance by operators, even if they do not have expertise in bio-electrochemical systems in general. MEC stacks of the prior art are constructed in a way that the necessary input gas for the reactions of all MEC cells is delivered to one inlet
30 typically at the first MEC cell and travels or flows through the subsequent MECs. The input gas is

thus used sequentially throughout the MEC cells for the respective reactions of the gas production process (e.g. methanation).

In the prior art, several problems arise from the use and operation of a MEC stack.

5 Firstly, a volumetric problem arises. Large volumes of input gas are necessary for substantial optimal reaction throughout all MEC cells, increasing both size and costs related to the MEC stacks.

A second problem relates to the efficiency of the reactions in MEC stacks. Inefficiencies are constantly perpetuated during a continuous operation of the MEC stacks of the prior art. The carbon feeding strategy for example does usually not meet the carbon source demand of the
10 microorganisms in each MEC cell. Consequently, the electron donors, e.g., hydrogen (reductive power) in the MEC cells are often unused or inefficiently used, which results in lower methane production and a substantially amount of unused hydrogen in the output gas.

Further problems are related to the changes in physico-chemical conditions for the microorganism(s)/strain(s) caused by the introduction of input gas to the system. The MEC stacks
15 of the prior art hence experience gradients in the physico-chemical conditions for the residing strain resulting in regions within the stack that do not provide optimal conditions for microbial metabolism or e.g. methane production leading to clearly reduced conversion of CO₂ and H₂ to methane compared with a theoretically calculated maximum output of such MEC stacks.

It is hence the aim of the present invention to provide a method and a system for carrying out
20 optimised methanogenic processes throughout a MEC stack, which at least partially solves or improves the inefficiency problems of the prior art.

Such a method and systems are defined by the independent claims for bio-electromethanogenesis employing MECs. The dependent claims specify embodiments of both the method and the systems, respectively.

25 Accordingly, a method to regulate the gas gradient in a process in a Microbial Electrolysis Cell (MEC) stack comprising at least two MEC cells is provided. The method comprises the steps of

a. Measuring :

- i. the current and voltage of MEC cells and/or MEC stack to determine the hydrogen production rate,
- ii. optionally, the pH value of the catholyte in the catholyte circuit, and/or
- iii. optionally, the oxidation reduction potential of the catholyte and/or
- 5 iv. optionally, the temperature of the catholyte
- b. determine an input gas quantity for the one or more gas inlet points based on the information assessed in step a);
- c. feeding the determined input gas quantity through one or more gas inlets points, thereby regulating the volumetric requirement for efficient methane production in the MEC stack;
- 10 d. and, optionally, regulating the physico-chemical conditions, e.g. the pH value and/or the temperature and/or the oxidation potential of the catholyte for efficient methane production in the MEC stack, and
- e. de-gassing the MEC stack through one or more degassing element located after a MEC cell of the MEC stack.
- 15 The present method provides improved reaction conditions for the residing microorganism and shows an improved efficiency in methane production for the bio-electromethanogenesis process throughout the whole MEC stack.

According to the present invention the term “gas gradient” should be understood as the variable amount or mass of the gas occupying a certain volume in the individual MEC but also the

20 interconnected MECs in the MEC stack. Additionally, “gas gradient” refers to gradients in the gas phase composition. Such gradient is dependent and variable by the physical parameters of pressure and temperature of the catholyte, but also by the biological parameters as microbial metabolism and availability of reactants.

A MEC stack of the present invention comprises at least two MEC cells but is not limited to two.

25 MEC stacks with 3, 4, 5, 6, 7, 8, 9, 10 or more MEC cells are also envisaged. The at least two MEC cells of a MEC stack share a catholyte circuit, which passes through the cathode compartments of the MEC cells. The catholyte is the fluid with which growth medium including also input gas(es)

are brought to the microorganism (strain(s)) and/or in which the gases produced in a MEC cell during a reaction are transported.

According to the method, the first step comprises measuring the current and cell voltage.

According to the invention the current and voltage of MEC cells and/or MEC stack to determine

5 the hydrogen production rate is measured in mol per second according to $HPR = CE \times e^{-1} \times N_A^{-1} \times I$.

Here, **HPR** denotes the hydrogen production rate, **CE** the Coulombic efficiency, **e** the elementary charge, **N_A** the Avogadro number, and **I** the current. The coulombic efficiency, given by the ratio of the number of electrons in the product, i.e. hydrogen, and the total number of electrons transferred (current x time / e), needs to be determined experimentally based on the MEC's

10 hydrogen mass balance for the operation voltage range of the MEC.

Additionally and/or alternatively, the hydrogen concentration within the cathodic compartment may be measured by means of a dissolved hydrogen sensor. The placement of the dissolved hydrogen sensor, i.e. before or/and behind and/or inside a MEC cell or stack is of importance for the regulation of the production process to determine the hydrogen production rate.

15 This measurement of the hydrogen concentration within the cathodic compartment, and according to further embodiments the optional measurement of the pH value of the catholyte, of the oxidation reduction potential of the catholyte and/or of the temperature of the catholyte, all allow to determine the reaction conditions in the MEC and hence allow to regulate, to improve and to predict the reaction processes and the consequent production capacity of the MEC in the

20 MEC stack.

According to some embodiments the methanogenic microorganisms in the MECs convert hydrogen and CO₂ into methane. The rate of production of methane of a single MEC cell depends on the ratio of hydrogen and CO₂ fed to the methanogenic microorganisms and on the physico-chemical conditions offered to the strains/microorganism.

25 Theoretically, a substantially optimal production of methane is achieved by the methanogenic microorganisms when they have access to 4 parts of hydrogen and 1 part of CO₂. Under ideal conditions this results in substantially 100% conversion of the educts to methane according to the present invention. The conversion rate is determined by the activity of the biocatalyst that

depends on the physico-chemical conditions in the MEC. It is hence the primary aim to guarantee substantial optimal conditions for the strain(s) to achieve optimized conversion rates.

According to the present invention one highly effective way of controlling these conditions is by monitoring and measuring the quantity of hydrogen generated (e.g. produced) in the MEC and
5 thus available for the further reactions. Such measurement is most effectively achieved by measuring the current and/or the voltage at the cathode compartment of one or more MECs as described above.

Depending on the current and/or voltage measured a theoretical quantity of hydrogen produced in the MEC cells can be calculated and a correspondent quantity of CO₂ is then provided to
10 achieve nearly substantial optimal reaction conditions and conversion rates.

Further factors which influence the physico-chemical conditions for the strain(s) are the pH value of the catholyte as well as the oxidation reduction potential. According to the method of the invention these additional measurements are also helpful for regulating and improving the physico-chemical conditions for the strain(s) in the catholyte

15 The catholyte should preferably have a pH value of between 6 and 9, in particular of between 7,5 and 8,5 and in particular of ca. 8. A pH value above or below will impede an optimal growth and metabolic functionality behind the methane production. Hence a proper balance is assisted by optional pH measurements of the presented method. The pH measuring system can be a commercially available pH sensor.

20 The oxidation reduction potential (ORP) in an aqueous solution, such as the catholyte, determined the tendency of the solution to gain or lose electrons. In a MEC cell electrical power is used to provide the potential difference between the anode and the cathode. At the anode water is electrochemically split into protons, electrons and oxygen. At the cathode electrons are used as reductive power, for instance with H₂ as electron carrier, to reduce electron acceptors, e.g.,
25 CO₂ to CH₄. The ORP measuring system can be a commercially available ORP sensor.

The pH measuring systems as well as the ORP measuring system are arranged on the catholyte circuit. These measuring systems can be e.g. encompassed in the degassing element. The measurements on the catholyte are hence made after the catholyte has been degassed.

It is relevant for an optimal generation of hydrogen and subsequently of methane to maintain the ORP at a defined value, preferably around or below -100 mV.

Also, the measurement and regulation of the temperature of the catholyte helps to improve an environment for the strains to improve conversion rate. The cathode side of a MEC cell generates
5 heat which warms up the catholyte. The catholyte running out of the cathode compartment is hence usually too warm for the microorganism in the MEC cell and also in the subsequently following MEC cells to efficiently convert CO₂ and H₂ into methane. Accordingly, the negative effects of increasing catholyte temperature limits negatively the size of the MEC stacks.

As described all the possible physico-chemical conditions measured in step a. influence
10 singularly and/or jointly the methanogenic reactions in the MEC cells or in the whole MEC stack. The quantity and quality of the gas comprising methane produced in the MEC stack is therefore at least partially dependent on the conditions in and characteristics of the catholyte in the individual MEC cells.

The next step of the method according to the present invention comprises determining an input
15 gas quantity for at least one gas inlet point based on the information assessed in step a).

Particularly, the quantity of input gas should be advantageously regulated depending on the amount of hydrogen produced in the MEC cells of the MEC stack, such as to have a ratio of hydrogen and CO₂, optimal for the strain(s).

Feeding the system and in particular the catholyte with an input gas, has also an effect on the pH
20 value, the ORP and the temperature of the catholyte and therefore on the physico-chemical conditions for the strain(s) in the cathode compartments.

Hence, based on the information gathered in step a) an overall quantity of input gas preferably required by the system is determined and the relative quantity of input gas needed to balance the system can be calculated. In particular it is determined how much input gas should be fed to
25 the system or optionally, should be fed to one or more gas inlets of the system.

Accordingly, the next step of the method comprises feeding the determined input gas quantity through at least one gas inlets point, optionally also at least two or more gas inlets point, thereby regulating the volumetric requirement for efficient methane production in the MEC. Furthermore,

in some embodiment feeding the determined input gas quantity also is used for regulating the pH value and/or the temperature and/or the oxidation potential of the catholyte and thereby improving reaction conditions for the production of methane.

5 Determining the input gas required for at least one or more gas inlets and feeding the input gas through at least one or more gas inlets, has proven to be particularly advantageous and results unexpectedly in synergistic effects.

For illustrative purposes, the method of the present invention comprising the feeding of an input gas at e.g. two or more gas inlets leads to efficient amounts of CH₄ also the required overall energy input is substantially reduced and in particular less voltage and/or current is needed for
10 the generation of hydrogen and the optimized operation, including cooling, of the MEC stacks, still resulting in a clearly more efficient methane production compared to any prior known bio-electromethanation set-ups.

Furthermore, it is an advantage that the electrode liquid interface area of the MEC cells herein also called “active electrode surface area” or just “active area”) increases. Through the
15 widespread distribution of input gas, the individual MEC cell experience on average less input gas, thus a lower gas gradient and at the same time a higher amount of liquid phase, hence more active area.

By providing an increase in active area, less stack voltage is required to drive a pre-defined current through the MEC cells of the MEC stack or a higher current, together with increased H₂
20 production through the MEC stack at a pre-defined voltage can be achieved. As such the overall energy consumption of the MEC stack is greatly decreased, without any loss in efficiency.

This improvement in power consumption can be achieved already by the presence of two gas inlets in the MEC stack and increases with the addition of more gas inlets in the MEC stack, e.g. one before each MEC cell. Therefore, according to the present method, the methanogenic
25 reaction process can be achieved using less power, minimizing hence its impact on the environment. Hence through the present method a more efficient methane production and less power consumption is achieved and smaller MEC cells can be construed and used.

Using one or more gas inlets for the input gas, e.g. two or more has the advantage of distributing the effect its input gas on the catholyte. For example, the effect on the catholyte’s pH created by

the local introduction of CO₂ is a decrease in pH value. Inputting the input gas on one single gas inlet as done in the prior art establishes non favorable pH values to support the bio-methanation reaction at the catholyte. The MEC cells located after the such gas inlet experience therefore disturbances in their physico-chemical conditions with negative consequences for the
5 conversion rate.

Inputting the gas on several gas inlet at different location of the MEC stack instead creates a better homogeneous distribution of the gas and diminishes the local impact of the input gas on the pH of the catholyte. As such it generates a better condition for the strain and hence better conversion rates.

- 10 Similar concepts, of course, apply with the regulation of temperature. Feed gas temperature usually deviates from the optimal temperature for the biological methanation reaction. Inputting it all at once at one inlet (as done in the prior art) will create a gradient in the temperature of the catholyte and the first MEC cell e.g. receiving colder catholyte demonstrate inefficient reactions.

- 15 Again, distribution of the input gas by inputting it at several inlets (e.g. at least two inlets) causes a more homogenous temperature distribution. The temperature of the catholyte circulating to the MEC cell shortly after one of the two or more inlets, therefore deviates less from the optimal conditions than in the prior art and the reaction is more efficient. It also minimizes the need for external heat generators and/or cooling elements hence minimizing production cost while having a more positive effect on the environment.

- 20 Similar efficiency advantages as described with respect to the measurement and effects of the pH value and temperature occur with the ORP. A low oxidation-reduction potential (ORP) in the growth medium is regarded as important to methanogenesis. This parameter can be control by the addition of a chemical reductant, such as Na₂S. The volume of CO₂ and its effect on pH may lead to higher stripping of the Na₂S as H₂S and hence in a reduction on its concentration. This
25 fact would raise the ORP until non favourable conditions. The culture conditions should suitably maintain a redox potential of about -100 mV or less.

Creating a substantial optimal environment for the strain (e.g. the methanogenic microorganism) has the consequence of higher methane conversions rate. Therefore, according to the present method more methane can be produced, and its production is more efficient.

A further advantage of the use of multiple gas inlets in the method is the smaller sized MEC cells which can be used with such optimizing method.

In the prior art, the input gas flows together with the growth medium through all the MEC cells connected in the MEC stack. This means that enough input gas needs to be provided at the first
5 MEC cell to fulfil the needs of all MEC cells for the methanation reaction. This causes the MEC cells to be bigger in size than necessary.

Due to feasible boundaries regarding conditions in the size of the MEC cells of the prior art the necessary quantity of input gas allowing an amount of gas for a substantial optimal reaction of the whole MEC stack cannot be provided without compromising the suitable reaction conditions.
10 All this causes a decrease in production efficiency regarding the methanogenic reaction in the MEC stack, and the potential capacity cannot be fully exhausted.

With the present invention and the present method to regulate the gas gradient in a bio-electromethanogenesis process such problems are overcome and minimized. In particular it becomes possible to overall feed more input gas into the system and as such have a higher
15 production rate of methane through more efficient reactions involved in the methanation process.

The last step of the method comprises de-gassing the MEC stack through at least one degassing element located after a MEC cell of the MEC stack. In this step a first gas – being a first part of the output gas - is being degassed at least at the last cell of the MEC stack. The first gas can for
20 example be methane but is not limited to it. It can also be a combination of different process gases produced during the reactions of the various MEC cells. The degassing of the catholyte can e.g. occur at a catholyte reservoir located after the last MEC cell.

It follows that according to the present method, the energy efficiency of the gas production e.g. methane production is enhanced, because resources are used more efficiently and substantially
25 fully as can be seen also in Figure 3. The present method and system, thereby, minimizes production cost through the effective use of resources, and also increase the quality of the produced gases (e.g. methane) as it allows a better controlling and regulation of the production process.

According to an embodiment step a) namely the measuring of at least one of the different parameters of the catholyte comprises measuring and/or calculation the quantity of hydrogen production in at least two MEC cells of the MEC stack as described above. This can be done for example by measuring the current in the respective cathode compartments.

- 5 As mentioned above, knowledge of the quantity of hydrogen produced is helpful to decide the substantial optimal quantity of the input gas (e.g. CO₂) required to be fed to the catholyte to achieve ideal reaction efficiencies. The measuring could for example be done at a first and a last MEC cell or at a first and a middle MEC cell, or at any two or more different MEC cells. Additionally, calculation can be based on the current.
- 10 Also, measurement and/or calculation of the hydrogen production of all MEC cell is intended and encompassed in the application, as mentioned according to the present method a more energy efficient process can be obtained, meaning higher current in the MEC cells are possible or the stack voltage can be reduced. Hence more hydrogen can be produced with a given electrical energy input. With the targeted addition of CO₂ based in this data, more methane can be
- 15 produced as well. In particular, by controlling the current through the voltage the hydrogen production in a MEC Cell and/or in a MEC Stack the can be regulated. As such the amount of hydrogen produced can be set and according to the present invention a targeted addition of CO₂ based on the amount of hydrogen can be provided thus increasing the efficiency of the MEC stack.
- 20 According to a further embodiment of the present method step a) comprises additionally measuring the pH value of the catholyte through a pH measuring system located before and/or after the two or more gas inlets points.

- If the pH measuring system is located before the gas inlet point, it is suitable for example to determine the required input gas quantity. The measuring system can be located for example in
- 25 a catholyte reservoir or directly on the catholyte circuit shortly before the gas inlet.

If the pH measuring system is after a gas inlet it is also useful to see the impact the input gas has on the pH value of the catholyte. This might then be used to determine the amount of input gas to be fed through another gas inlet, and/or it might serve as a control mechanism to ensure that

the amount of input gas fed in through the gas inlet before the pH measuring system, indeed, had the expected effect on the pH value of the catholyte.

Also, combinations of locations are encompassed by the current application. The pH measuring device could be located before some of the gas inlets and/or after other gas inlets. Also, pH
5 measuring system before and after a or each gas inlet are envisaged.

As such, these are mechanism to control and/or regulate the physico-chemical conditions of the catholyte to stabilise and improve growth conditions for the microorganisms or strain(s).

According to an even further embodiment the method comprises a step of further degassing the MEC stack with further degassing elements. The further degassing elements could for example be
10 positioned after some or all the MEC cells, such as to have a degassing effect of an output gas (e.g. methane) immediately after its production at an individual MEC cell of the stack of MECs.

In this way, some gases such as the product gases are extracted from the system at one or several locations. By extracting gases at several locations of the MEC stack, a minimization of necessary storage volume of the respective gas in a respective MEC cell is achieved and at the same time
15 the active area in the respective MEC is increased.

For example, produced methane could be degassed out of each MEC cell instead of being transported by catholyte through all the fluidly connected MEC cells. As such the MEC cells do not need additional volume to hold the methane produced by antecedents MEC cells. The MEC cells hence can be made smaller, or the additional volume can be used more efficiently for example
20 for the additional conversion of hydrogen and/or carbon dioxide into methane. This substantially increases production efficiencies.

Degassing can hence be used to further stabilize the conditions and regulate the catholyte such as to create substantial optimal growth and/or methanation condition for the strain(s).

Furthermore, degassing the MEC stack at different locations has also an effect on the physico-chemical conditions for the strains. By degassing the MEC stack, the pH value, the temperature
25 and/or the ORP are influenced through the exit of the gases and hence improved or optimized conditions for the strains can be achieved.

The present method to regulate the gas gradient hence maximizes the control and regulation of the physico-chemical conditions of the catholyte and hence of the methanation reactions in each MEC cell of the MEC stack. The many degrees of freedom in the physico-chemical conditions for the microorganism linked to the efficiency of methane production are hence influenced by the presence of one or more gas inlets and of one or more the degassing elements.

The present method and its embodiments therefore produce methane more efficiently and with substantial less energy.

According to this invention also systems through which the regulation of the gas gradient in a bio-electromethanogenesis process can be achieved are provided.

According to one aspect of the invention a MEC stack in a bio-electromethanogenesis plant is hence provided. The MEC stack comprises at least two MEC cells, wherein each MEC cell comprises a cathode compartment and an anode compartment. The MEC cells are fluidly connected in parallel or in series, and the MEC stack comprises at least one catholyte circuit connecting the cathode compartments of the two or more MEC cells of the MEC stack. The invention is characterised in that two or more gas inlets are located within the at least one catholyte circuit.

According to the current application a bio-electromethanogenesis plant is a system, a plant, a container, a facility, or similar in which a process to produce methane by using at least one MEC stack is conducted.

As mentioned, a MEC stack according to the present invention comprises at least two MEC cells which are fluidly connected. Each MEC cell comprises a cathode compartment and an anode compartment. The MEC cell are fluidly connected either in parallel or in series to each other.

In this application, when discussing the “connection of the MECs” the fluid connection in parallel or in series through at least one catholyte circuit is intended. A fluid connection between two MEC cells according to the present invention is a connection in which at least one fluid (e.g. a catholyte and/or gas) can pass through and reach the connected MEC cells. The fluid connection can be achieved for example using conduits.

MEC cells in a MEC stack are also electrically connected, however this invention is not referring to any electrical connection if not explicitly stated.

According to this invention, the MEC stack is not limited to MEC cells being connected in parallel or in series exclusively. Also stacks in which at least two groups of MEC cells are connected in series and in which the at least two groups are parallelly connected to each other are envisaged.

According to the invention the MEC stack comprises at least one catholyte circuit connecting the cathode compartments of two or more MEC cells of the MEC stack. The catholyte circuit transports through the catholyte the growth medium required by the methanogenic microorganism to be sustained and metabolically active. The catholyte circuit comprises catholyte and for example one or more gases, which are fed to the cathode compartments of the MEC cells.

According to the present invention the MEC stack comprises at least one catholyte circuit, meaning it can comprise more than one catholyte circuits, for example 2, 3, 4, 5, 6, 7 or more circuits. Some MEC cells of the MEC stack might be fluidly connected by a first catholyte circuit and some MEC cells of the MEC stack might be fluidly connected by a second catholyte circuit. The first and second catholyte circuits can also be fluidly connected to each other according to further embodiments.

According to some examples each odd “numbered” MEC cell (e.g. the first, third, fifth etc.) might be connected by a first catholyte circuit, while all the even numbered MEC cells might be connected by a second catholyte circuit (e.g. the second, fourth, sixth etc.). Any other combinations are also considered and envisaged in the present application.

According to the present invention, the MEC cells in a MEC stack are conceptually arranged, such that each MEC stack comprises a first and a last MEC cell, as well as optionally a second, a third, a fourth MEC cell, etc..

According to one embodiment, the MEC stack comprises at least two gas inlets located within the at least one catholyte circuits. As mentioned above with respect to the claimed method, it has been proven surprisingly advantageous to feed the system with an input gas at e.g. two different locations within the MEC stack and/or within the catholyte circuits.

Distributing the volume of the input gas throughout the circuit efficiently uses the size and volume of the MEC cells at hand and maximises the active area of the various MEC cells and consequently the efficiency of the electro-methanation reaction.

5 By maximizing the active area of the MEC cells, through minimizing the quantity of input gas in different cells, higher current at equal voltage is produced and/or a lower voltage is required to drive the same current and the overall power consumption of the MEC stack is minimized and substantially reduced compared with theoretical calculations thereon.

Further advantages are the better regulation of the catholyte with respect to the pH value, the oxidation-reduction potential of the catholyte and/or the temperature of the catholyte, and thus
10 a better regulation of the physico-chemical conditions for the strains in the MEC cells.

Feeding the gas at different location distributes its impact on the catholyte and at the same time minimizes variances near a single gas inlet point. Due to the improved conditions for the strains a surprisingly high efficiency of the methanation reaction in the MEC cell can be achieved as the methanogenic organisms are no longer hampered or confronted with a peak increase/decrease
15 in pH value, temperature and/or ORP of the catholyte through just a single inlet (as in the prior art).

According to further embodiments, the at least two gas inlets according to the present invention can be located at any stage within the catholyte circuit, although it has proven to be advantageous if at least one gas inlet is located before a first MEC cell.

20 According to further embodiments more than two gas inlets are used. According to one such embodiment at least one of the gas inlets is located at one or more individual MEC cells of the MEC stack. According to a further embodiment, a gas inlet can be located before e.g. every second MEC cell.

In this way, for example, the volume of input gas necessary for a substantial optimal reaction in
25 two subsequent MEC cells is inserted into the catholyte before the first of the two MEC cells. After the second MEC cell the input gas has been entirely used up for the methanation process. This can be repeated for every two subsequent MEC cells of the stack of MEC cells

Accordingly, also a gas inlet before each MEC cell is also envisaged. In such an embodiment the gas inserted into the catholyte before each MEC cell corresponds to the substantially optimal requirement of the single MEC cell. This is an efficient way of feeding an input gas to the catholyte and consequently to the MEC cell for its conversion to methane. In this way the conversion of the input gas is efficiently regulated, its impact on the catholyte is considered and efficiently controlled and methane production is increased due optimised growth and methanation conditions for the bio-catalyst e.g. the strains. All this is achieved with less energy input than in the MEC stack of the prior art.

According to an even further embodiment the MEC stack comprises at least one gas inlet within the cathode compartment of the one or more individual MEC cells. In some embodiments it might comprise two or more gas inlets per catholyte compartment.

In this embodiment, the gas input is inserted directly into the catholyte inside the cathode compartment. By doing so, the efficiency in the MEC cell can further be regulated, as the impact of the input gas on the physico-chemical conditions of the catholyte can be better controlled.

According to a further embodiment each gas inlet comprises a respective flow controller to selectively regulate the gas input from the gas source. According to other embodiments, only some flow controllers are arranged in the MEC stack.

The flow control can for example be a valve or similar. The flow control might also encompass computerized means which evaluate the data received from the measurements of the above-described method or directly from sensors located at various location of the MEC stack and regulate the amount of input gas passing through each of the gas inlets.

According to a further embodiment of the present invention the MEC stack comprises at least one degassing element to extract at least a first gas from the MEC stack, wherein at least one of the at least one of the degassing elements is located after a last MEC cell of the MEC stack.

This degassing element is used to extract at least a first gas from the MEC stack, wherein the first gas might be any product gas produced in the MEC stack during catalysed reactions (e.g. methane and/or hydrogen) and/or any other gas already present in the MEC stack. After extraction of the first gas the catholyte can be recirculated through the catholyte circuit.

The use of at least one degassing element in the MEC stack system is a further way to efficiently manage and operate the MEC stack. By using at least one degassing element, but in particular two or three or more degassing elements, it is possible to extract the first gas and at the same time create volumetric space in the MEC cells for new input gas and/or for the conversion of additional hydrogen as well as higher hydrogen production.

The degassing element is further used as a regulating system for the physico-chemical conditions of the strains. Degassing has an effect on the pH value, the temperature and the ORP of the catholyte and hence on the conditions of the strains. By degassing the MEC stack at more locations these physico-chemical conditions can be better regulated and as such a better and more efficient methane production can be achieved.

Similarly, as explained with regards to the method, the active phase in the several MEC cells is increased and the MEC stack requires less energy to operate being as such more environmentally friendly.

As mentioned above, according to a further embodiment the one or more degassing element are located after one or more of the other MEC cells. In this way, the product gases as well as other gas(es), which may be considered part of the first gas according to the present invention, can be extracted immediately after production and don't need to pass through all the different MEC cells and be degassed at the last MEC cell and as such also maximizing the active surface of the MEC cells. Even less energy is hence required for an efficient methanation reaction and corresponding methane production.

According to a further embodiment the MEC stack comprises at least one device selected from of a pH measuring system, a ORP measuring system, a temperature measuring system, and a current/voltage measuring system. According to a further embodiment the pH measuring system and/or the ORP measuring system and/or the temperature measuring system and/or the current measuring system are located before and/or after at least one gas inlet.

As already mentioned with respect to the method the reaction efficiency of the MEC stack and of each MEC cell is influenced by one or several of the above-mentioned values. A gas input through a gas inlet or a gas output through the degassing element destabilize these values, by for

example lowering or increasing the temperature of the catholyte and/or the value of the pH and/or the ORP Value.

Measuring system are therefore required which measure these values and which permit to evaluate how much of an input gas should be inputted through a gas inlet and how much of gas
5 output should be extracted at the degassing element.

Furthermore, some of the measuring devices can be located before a gas inlet on the catholyte circuit, such as to measure the values of the catholyte before being fed with an input gas. In this way, regulation of these values in the catholyte can be controlled and modulated.

The measuring system can also be located immediately after a gas inlet at the catholyte circuit.
10 This system would therefore function as a control mechanism to control that these values (e.g. pH, temperature, ORP) have indeed had the expected effect on the catholyte which will flow to and through one or more MEC cells.

According to the present invention and in line with the above-mentioned method, a MEC with multiple gas inlets and at least one degassing element has been described.

15 A further alternative providing substantial the same benefits and technical effects as the system with two or more gas inlet, is a system with one gas inlets and two or more degassing elements.

Accordingly, a MEC stack in a bio-electromethanogenesis plant comprising at least two MEC cells, wherein each MEC cell comprises a cathode compartment and an anode compartment. The MEC cells are fluidly connected parallelly or in series and the MEC stack comprises at least one
20 catholyte circuit for a catholyte, connecting the cathode compartments of two or more MEC cells of the MEC stack.

The MEC stack comprises in this embodiment one gas inlet for an input gas located at a first MEC cell of the MEC stack, wherein the MEC stack is characterized in that it comprises at least two degassing elements for extracting at least one first gas. At least one degassing elements is also
25 located after the last MEC cell of the MEC stack.

In this embodiment, the input gas is being fed at a first MEC cell. The entire quantity of input gas required by the whole MEC stack is fed through the first gas inlet located at the first MEC cell. As the MEC stack in this embodiment comprises at least two degassing elements one degassing

element is located at the last MEC cell to extract the gases at the end of the MEC Stack. The at least one other degassing element can be located at any suitable place along the MEC stack in particular and for example at an early or middle MEC cell.

By having several degassing elements, it is possible to increase the active surface of the MEC cells and hence lowering the voltage required and/or increasing the current for the hydrogen generation, which is required for the reaction processes, therefore minimizing power consumption of the MEC stack.

Furthermore, degassing the MEC stack at different position through two or more degassing elements has the advantage of stabilizing the gas gradient in the catholyte. A regulated degassing can assist in creating substantial optimal physico-chemical conditions for the strain(s) as described above.

According to another embodiment of the present invention hence at least one de-gassing element is located after one or more of the other MEC cells.

A further inventive idea is to expand the various MEC stacks into a MEC module comprising two or more MEC stacks, each comprising at least two MEC cells. The MEC stacks are fluidly connected to each other in the MEC module, whereby they could be fluidly connected both in series or parallelly.

In this way big plants can be provided with an increase in production and at the same time ameliorating efficiency caused by the above-mentioned features and advantages of the inventive MEC stacks.

According to the present invention also a single MEC is provided as individualisable cell for a bio-electromethanogenesis reaction. The MEC cell are suitable for use in a MEC stack and in MEC models in a corresponding bio-electromethanogenesis plant.

According to the present invention they are characterised by either one gas inlet for an input gas and two or more degassing elements or alternatively, two or more gas inlet for an input gas and one or more degassing elements. Thus, as mentioned above with respect to the MEC stack, also each MEC cell can have at least two gas inlets. Both alternatives have a regulatory effect on the catholyte and hence a direct effect on the efficiency of production of methane in the MEC cells.

Short description of the Figures and Examples

Specific embodiments of the method and the system will now be disclosed through the following figures, in which:

Figure 1a shows a schematic MEC stack with two MEC cells comprising two gas inlets and one degassing element according to one exemplary embodiment of the present invention.

Figure 1b shows a schematic of an alternative more compact embodiment of the MEC stack with two MEC cells comprising two gas inlets and one degassing element according to one exemplary embodiment of the present invention.

Figure 2 shows a schematic MEC stack with two MEC cells comprising one gas inlets and two degassing elements according to another exemplary embodiment of the present invention.

Figure 3 is a graph showing the methane production rate of methane depending on the number and position of gas inlets in the example of Figures 1a and 1b. Although for all three experiments the same amount of input gas (CO₂ supply) was used already this simple experiment shows that different locations of one or more gas inlets have dramatic consequences on the methane production rate of a MEC stack.

Figure 4 shows an exemplary schematic composition of the cathodic compartments of a MEC stack of the prior art with n-MEC cells. The gas inlet is before the first MEC and as it is depicted the total amount of gas is fed into the MEC stack via said inlet, which leads to the above described volumetric problem that in said first MEC the percentage of liquid phase (corresponding to the active area) is quite restricted, while a high percentage of the MEC cathode compartment volume is occupied by the educt (CO₂, H₂) and product gas (CH₄) with the fraction of product gas increasing with increasing cell number.

Figure 5 shows an exemplary schematic composition of a MEC stack with n-MEC cell cathodic compartments comprising a gas inlet before each MEC cell and one degassing element at the last MEC cell, according to an exemplary embodiment of the present invention.

Figure 6 shows an exemplary schematic composition of a MEC stack with n-MEC cell cathodic compartments comprising a gas inlet before each MEC cell and one degassing element after each MEC cell, according to an exemplary embodiment of the present invention.

As can be seen in **Figure 1a and 1b**, this exemplary embodiment of a MEC stack 1 comprises two MEC cells 10a, 10b. Each MEC cell 10a, 10b comprises a cathode 12a, 12b and an anode 14a, 14b. The left part of Figure 1a and 1b shows the anode side of the MEC Stack which will not be described in detail. The cathode side of the MEC stack 1 comprises a catholyte circuit 18 which
5 fluidly connects the two MEC cells 10a, 10b.

The MEC stack 1 of **Figure 1a and 1b** comprises two gas inlets 22a and 22b, in which a respective gas source 20a, 20b is used to feed an input gas to the catholyte. The gas sources 20a and 20b comprises carbon dioxide CO₂ in this example but are not limited to these. As can be seen, the two gas inlets are arranged before each MEC cell 10a, 10b, respectively.

10 On the catholyte circuit 18 and after the second MEC cell 10b, a degassing element 30 is located to degas the catholyte of the catholyte circuit 18. Further, pH measuring systems 32 and ORP measuring system 34 are arranged on the catholyte circuit 18. These measuring systems are in this example encompassed in the degassing element 30. The measurements on the catholyte are hence made after the catholyte has been degassed.

15 As can be seen in **Figure 2**, this exemplary embodiment of a MEC stack 1 comprises two MEC cells 10a, 10b. Each MEC cell 10a, 10b comprises a cathode 12a, 12b and an anode 14a, 14b. The left part of Figure 2 shows the anode side of the MEC Stack which will not be described here.

The cathode side of the MEC stack 1 comprises a catholyte circuit 18 which fluidly connects the two MEC cells 10a, 10b. The MEC stack of **Figure 2** comprises one gas inlets 22a with a respective
20 gas source 20a. In this example the gas source 20a is carbon dioxide. According to this embodiment the MEC stack 1 comprises two degassing elements 30a and 30b both arranged on the catholyte circuit 18. The first degassing element 30a is located after the first MEC cell 10a, while the second degassing element 30b is located after the second (or last) MEC cell 10b.

Further, pH measuring systems 32 and ORP measuring system 34 are arranged on the catholyte
25 circuit 18. These measuring systems are in this example encompassed in the degassing element 30b. The measurements on the catholyte are hence made after the catholyte has been degassed.

Figure 3 shows the methane conversion rate of the system of Figure 1a with two different CO₂ feed configurations.

The first column shows the methane conversion with just one gas inlet 22a of Figure 1a – this represents the prior art. The second column shows the methane conversion with two gas inlets 22a, 22b, according to the exemplary embodiment of the present invention in Figure 1. As can be seen from the graph, the methane conversion is at its highest when two gas inlets 22a, 22b have been arranged in the MEC stack 1. As described before, this is due to the better physico-chemical conditions for the strains through a distributed and targeted input gas supply.

Figure 4 shows the distribution of gases and catholyte (liquid phase) in the MEC cells of a MEC stack of the prior art. As can be seen from this illustration, the input gas (in this example CO₂) is fed at a single gas inlet **22a** point before the first MEC cell. The first MEC cell has further a liquid phase which is of limited volume and shows also the hydrogen produced through electrolysis. In the first MEC cell a portion of the CO₂ is converted into methane (CH₄) and the methane as well as the remaining CO₂ is transferred by the catholyte in the catholyte circuit to the second MEC cell catholyte compartment 12b.

In the second MEC cell further reactions occur, and further methane is produced, which with the remaining CO₂ is transmitted to the third MEC cell catholyte compartment 12c. This process continues until the last MEC cell catholyte compartment 12n in which most of the gas is the produced methane and there is enough CO₂ for at least one more reaction in the last MEC cell catholyte compartment 12b to produce methane. The produced methane 97 is then degassed after the last MEC cell through the degassing element 30a. The remaining catholyte is then send back through the circuit to the first MEC cell, where it is enriched with input gas again.

As can be seen, in this system of the prior art, the MEC cells are confronted with big quantities of input gas (e.g. CO₂) and quite some energy and efficiency is wasted transporting both the produced methane and the remaining CO₂ through all MEC cells.

The liquid phase in this figure represents the active area of a respective MEC cell.

Figure 5 shows the distribution of gases and material in the MEC cells of a MEC stack according to an exemplary embodiment of the present invention in which a respective gas inlet is located before each MEC cell. The MEC cell catholyte compartments 12a to 12n are connected by a catholyte circuit 18, but this time before each MEC cell a gas inlet 22a to 22n is located before the respective MEC cell catholyte compartments 12a to 12n. As can be seen from the distribution in

the first MEC cell, the average liquid phase is substantially bigger than in the example of Figure 4. Therefore, the active area in the MEC cells of Figure 5 is increased and more efficient reactions with less power consumption can be achieved.

- Through the gas inlet 22a the required quantity of CO₂ for the methanation process in MEC cell catholyte compartment 12a is fed to the MEC cell catholyte compartment 12a. Through the gas inlet 22b the required quantity of CO₂ for the methanation process in MEC cell catholyte compartment 12b is fed to the MEC cell catholyte compartment 12b. Same applies for the remaining MEC cells. As such the methane portion in the second MEC cell is bigger than the methane portion in the second MEC cell of the Figure 4.
- 10 In **Figure 5**, the liquid phase in the MEC cell is decreasing between MEC cells. The last MEC cell catholyte compartment 12n has the complete amount of methane produced 98 in the MEC cell catholyte compartment s before 12a to 12n-1, the input carbon dioxide required for the last reaction of the MEC cell catholyte compartment 12n and the lowest amount of liquid phase of all MEC cells in the MEC stack. In this embodiment due to the overall increased liquid phases and
- 15 hence the larger active areas, energy consumption is minimized compared to the example according to Figure 4. Accordingly, the whole MEC stack is more efficient.

- Figure 6** shows a further development of an exemplary MEC stack according to the present invention. The MEC stack of **Figure 6** is similar to the one of Figure 5 with the exception, that further to several gas inlet before various MEC cell, the MEC stack comprises several degassing
- 20 elements after various MEC cell. In this way, as can be taken form the figure, the liquid phase is nearly constant at a high level in each MEC cell catholyte compartment therefore increasing the active area constantly. In this example power consumption is less than in the MEC stack of Figure 5 and methane production 99a to 99n is still more efficient.

- It has surprisingly found that even with an energy consumption, which is less for the whole MEC
- 25 stack compared with the sums of the energy consumption of all individual MEC cell a more efficient methanation rate and a higher methane production per unit energy can be upheld.

Patent Claims

1. Method to regulate the gas gradient in a bio-electromethanogenesis process in a Microbial Electrolysis cell (MEC)-stack comprising at least two MEC cells, the method comprising the steps of
 - 5 a. Measuring in the cathode compartments the stack current and/or voltage of the MEC and/or MEC-stack;
 - b. Determine an input gas quantity for at least one gas inlet point based on the information assessed in step a);
 - c. Feeding the determined input gas quantity through at least one gas inlet point, thereby
10 regulating the volumetric requirement for efficient methane production in the system and
 - d. De-gassing the MEC stack through one or more degassing element located after a MEC cell of the MEC stack.
2. Method according to claim 1, wherein step a) further comprises measuring at least one of:
 - (i) the pH value of the catholyte in the catholyte circuit,
 - 15 (ii) the oxidation reduction potential of the catholyte
 - (iii) the temperature of the catholytethereby regulating in step c) the pH value and/or the temperature and/or the oxidation potential of the catholyte
3. Method according to claim 2, wherein step a) comprises measuring the pH value of the
20 catholyte through a pH measuring system located before and/or after the two or more gas inlets points.
4. MEC stack (1) in a bio-electromethanogenesis plant comprising:
at least two MEC cells (10a, 10b),
wherein each MEC cell (10a, 10b) comprises a cathode compartment (12a, 12b) and an
25 anode compartment (14a, 14b);

wherein the MEC cells (10a, 10b) are fluidly connected parallelly or in series; and

wherein the MEC stack comprises at least one catholyte circuit (18), connecting the cathode compartments (12a, 12b) of two or more MEC cells (10a, 10b) of the MEC stack.

characterized in that

- 5 two or more gas inlets (22a, 22b) are located within the at least one catholyte circuit (18).
5. MEC stack (1) according to claim 4, comprising at least one gas inlet (22a, 22b) at one or more individual MEC cells (10a, 10b) of the MEC stack (1).
6. MEC stack (1) according to claim 5 comprising at least one gas inlet (22a, 22b) within the cathode compartment (12a, 12b) of the one or more individual MEC cells (10a, 10b).
- 10 7. MEC stack (1) according to any of claims claim 4 to 6, wherein each gas inlet (22a, 22b) comprises a respective flow controller to selectively regulate the gas input from the gas source (20a, 20b).
8. MEC stack according to any of claims 4 to 7, wherein the MEC stack (1) comprises at least one de-gassing element (30) to extract at least a first gas /one of the process gases from the
- 15 MEC stack (1), wherein one of the de-gassing elements (30) is located after a last MEC cell of the MEC stack.
9. MEC stack according to claim 8 wherein one or more de-gassing element are located after one or more of the other MEC cells.
10. MEC stack (1) according to any of the claims 4 to 9 comprising at least one device selected
- 20 from of a pH measuring system (32), a ORP measuring system (34), a temperature measuring system, a volume measuring system, a current measuring system.
11. MEC stack (1) according to claim 10 wherein the pH measuring system and/or the ORP measuring system and/or the temperature measuring system and/or the volume measuring system and/or the current measuring system are located before and/or after at
- 25 least one gas inlet (22a, 22b).
12. A MEC stack (1) in a bio-electromethanogenesis plant comprising:

at least two MEC cells (10a, 10b),

wherein each MEC cell (10a, 10b) comprises a cathode compartment (12a, 12b) and an anode compartment (14a, 14b);

wherein the MEC cells (10a, 10b) are fluidly connected parallelly or in series; and

- 5 wherein the MEC stack comprises at least one catholyte circuit (18) for catholyte, connecting the cathode compartments (12a, 12b) of two or more MEC cells (10a, 10b) of the MEC stack.

the MEC stack (1) comprising one gas inlet (22a) for an input gas located at a first MEC cell (10a) of the MEC stack

10 **characterized in that**

the MEC stack (1) comprises at least two de-gassing elements (30a, 30b) for extracting at least one output gas, one of de-gassing element (30a, 30b) being located after a last MEC cell (10b) of the MEC stack (1).

13. The MEC stack (1) according to claim 12 wherein at least one de-gassing element (30a, 30b)
15 is located after one or more of the other MEC cells.

14. A MEC module (100) comprising two or more MEC stacks (10a, 10b) according to any of the above claims 6 to 16, the two or more MEC stacks (10a, 10b) being fluidly connected through the catholyte circuit (18).

15. A MEC cell for use in a bio-electromethanogenesis plant comprising one gas inlet for an
20 input gas and two or more degassing elements or comprising two or more gas inlet for an input gas and one or more degassing elements.