

**MODULAR ELECTROLYZER CELL AND PROCESS TO CONVERT CARBON DIOXIDE TO
GASEOUS PRODUCTS AT ELEVATED PRESSURE AND WITH HIGH CONVERSION RATE**

Field of the invention

The present invention relates to the field of generating gas-phase products at
5 elevated pressure and with high conversion rate via electrolysis of gaseous carbon dioxide.
The invention also relates, thus, to a novel modular electrolyzer cell to perform the
electrolysis, and hence to convert carbon dioxide gas into various gas-phase products,
preferentially ready to be used in further industrial processes as feedstock.

Background art

10 Carbon dioxide (CO₂) is a greenhouse gas; hence, using renewable energy to con-
vert it to transportation fuels and commodity chemicals is a value-added approach to sim-
ultaneous generation of products and environmental remediation of carbon emissions. The
large amounts of chemicals produced worldwide that can be potentially derived from the
electrochemical reduction (and hydrogenation) of CO₂ highlight further the importance of
15 this strategy. Electrosynthesis of chemicals using renewable energy (e.g. solar or wind en-
ergy) contributes to a green and more sustainable chemical industry. Polymer-electrolyte
membrane (PEM) based electrolyzers are particularly attractive, due to the variety of pos-
sible CO₂ derived products. Several industrial entities are interested in such technologies,
ranging from energy/utilities companies through cement producing and processing firms to
20 oil and gas companies.

Similarly to PEM based water electrolyzers (i.e. H₂/O₂ generators), a typical con-
figuration of a PEM based CO₂ electrolyzer consists of two flow-channels, one for the
anolyte and another for the catholyte, separated by an ion-exchange membrane which is in
direct contact with the catalysts. The cathode electrocatalyst is immobilized on a porous
25 gas diffusion layer (GDL), which is typically in contact with a flowing liquid catholyte,
while CO₂ gas is also fed through the GDL. This arrangement might overcome some of the
known problems of the field, namely: (i) current limitation due to the low concentration of
CO₂ at the electrode; (ii) H⁺ crossover from the anode through the membrane, and conse-
quent acidification of the catholyte, resulting in increased H₂ evolution selectivity; (iii) dif-
30 fusion of products to the anode, where they are oxidized (product crossover). Although no

such instrument is commercially available on the industrial scale at the moment, most components thereof (i.e. the GDLs and catalysts), as well as laboratory size setups (~5 cm² electrode size) are already available. Nevertheless, the structure of PEM based CO₂ electrolyzers and the operational conditions must be carefully optimized in the case of CO₂ electrolysis.

A comprehensive review on PEM based CO₂ electrolysis is provided e.g. in Progress in Energy and Combustion Science 62 (2017) pp. 133-154, wherein the parameters that influence the performance of flow CO₂ electrolyzers is discussed in detail. The analysis spans the basic design concepts of the electrochemical cell (either microfluidic or membrane-based), the employed materials (e.g. catalysts, support, etc.), as well as the operational conditions (e.g. type of electrolyte, role of pressure, temperature, etc.).

European Published Patent Appl. No. 3,375,907 A1 discloses a carbon dioxide electrolytic device in the form of a single stack electrolyzer that comprises an anodic part including an anode which oxidizes water or hydroxide ions to produce oxygen; a cathodic part including a cathode which reduces carbon dioxide to produce a carbon compound, a cathode solution flow path which supplies a cathode solution to the cathode, and a gas flow path which supplies carbon dioxide to the cathode; a separator which separates the anodic part and the cathodic part; and a differential pressure control unit which controls a differential pressure between a pressure of the cathode solution and a pressure of the carbon dioxide so as to adjust a production amount of the carbon dioxide produced by a reduction reaction in the cathodic part.

U. S. Published Patent Appl. No. 2018/0274109 A1 relates to a single stack carbon dioxide electrolytic device equipped with a refresh material supply unit including a gas supply unit which supplies a gaseous substance to at least one of the anode and the cathode; and a refresh control unit which stops supply of the current from the power supply and supply of carbon dioxide and an electrolytic solution, and operates the refresh material supply unit, based on request criteria of a cell output of the electrolysis cell.

U. S. Published Patent Appl. No. 2013/0105304 A1 relates to methods and systems for electrochemical conversion of carbon dioxide to organic products including formate and formic acid. An embodiment of the system includes a first electrochemical cell

including a cathode compartment containing a high surface area cathode and a bicarbonate-based liquid catholyte saturated with carbon dioxide. The system also includes an anode compartment containing an anode and a liquid acidic anolyte. Said first electrochemical cell is configured to produce a product stream upon application of an electrical potential
5 between the anode and the cathode. A further embodiment of the system may include a separate second electrochemical cell similar to the first one and in fluid connection therewith.

U. S. Published Patent Appl. No. 2016/0369415 A1 discloses catalyst layers to be used in electrochemical devices, in particular, for electrolyzers, the feed of which
10 comprises at least one of CO₂ and H₂O. The catalyst layers comprise a catalytically active element and an ion conducting polymer. The ion conducting polymer comprises positively charged cyclic amine groups. The ion conducting polymer comprises at least one of an imidazolium, a pyridinium, a pyrazolium, a pyrrolidinium, a pyrrolium, a pyrimidium, a piperidinium, an indolium, a triazinium, and polymers thereof. The catalytically active
15 element comprises at least one of V, Cr, Mn, Fe, Co, Ni, Cu, Sn, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Hf, Ta, W, Re, Ir, Pt, Au, Hg, Al, Si, In, Tl, Pb, Bi, Sb, Te, U, Sm, Tb, La, Ce and Nd.

U. S. Published Patent Appl. No. 2017/0321334 A1 teaches a membrane electrode assembly (MEA) for use in a CO_x reduction reactor. The MEA has a cathode layer
20 comprising reduction catalyst and a first ion-conducting polymer, as well as an anode layer comprising oxidation catalyst and a second ion-conducting polymer. Between the anode and cathode layers, a PEM comprising a third ion-conducting polymer is arranged. The PEM provides ionic communication between the anode layer and the cathode layer. There is also a cathode buffer layer comprising a fourth ion-conducting polymer between the
25 cathode layer and the PEM, the cathode buffer. There are three classes of ion-conducting polymers: anion-conductors, cation-conductors, and cation-and-anion-conductors. At least two of the first, second, third, and fourth ion-conducting polymers are from different classes of ion-conducting polymers.

International Publication Pamphlet No. WO2017/176600 A1 relates to an
30 electrocatalytic process for CO₂ conversion. The process employs a novel catalyst combination that aims to overcome one or more of the limitations of low rates, high

overpotentials and low electron conversion efficiencies (namely, selectivities), low rates for catalytic reactions and high power requirements for sensors. The catalyst combination or mixture includes at least one catalytically active element in the form of supported or unsupported particles wherein the particles have an average particle size between about 0.6 nm and 100 nm, preferably between 0.6 nm and 40 nm, and most preferable between 0.6 nm and 10 nm. The catalyst combination also includes a helper polymer that can contain, for example, positively charged cyclic amine groups, such as imidazoliums or pyridiniums. The catalyst combination of a catalytically active element and a helper polymer are very useful when used in the cathode catalyst layer of a single stack electrochemical cell for conversion of CO₂ to various reaction products.

U.S. Patent No. 10,208,385 B2 discloses a carbon dioxide electrolytic device with a single stack electrolyzer cell to convert CO₂ into various products, especially CO, wherein said cell includes a cathode, an anode, a carbon dioxide supply unit, an electrolytic solution supply unit, and a separator to separate said cathode and anode from one another. Besides the cell, the carbon dioxide electrolytic device further comprises a power supply; a reaction control unit which causes a reduction reaction and an oxidation reaction by passing an electric current from the power supply to the anode and the cathode. Said cell is fed with gaseous CO₂ on the cathode, and with a liquid electrolyte on at least the anode side. The gas and the liquid(s) are distributed within the cell through gas and liquid flow-paths, respectively, which are formed in the cathode and the anode current collectors.

As is clear from the aforementioned, most of the precedent art in the field of CO₂ electrolysis focuses on the development of new catalysts to enhance activity and product selectivity using single stack constructions. At the same time, in a simple batch-type electrochemical cell the maximum achievable rate for the reaction is often limited by the low solubility (~30 mM) of CO₂ in water. Similar problems arise when a solution (catholyte) is fed to the cathode of a continuous-flow electrolyzer, hence direct CO₂ gas-fed (i.e. no electrolyte) electrolyzer cells would be preferred.

Hence, there would be a need for increasing the CO₂ conversion rate to a level of practical significance. Putting this another way, to overcome mass-transport limitations, there would be a need for a continuous-flow, direct CO₂ gas-fed setup and process to

perform electrochemical CO₂ reduction with high conversion rate (e.g., current density of at least 150 mA cm⁻²).

There is a wide consensus in the field that to drive this process in an economically attractive way, it is important to produce (i) any product as selectively as possible; (ii) products of economic value; and (iii) products that are easy to separate. To achieve these

- High current density (which translates to high reaction rate);
- High Faradaic efficiency for the desired product(s) (i.e. large fraction of the invested total current ($\sum_i j_i$) is used for product formation (j_{product}), hence high selectivity appears towards a given product), here

$$\varepsilon_{\text{Faradaic, product}} = \frac{j_{\text{product}}}{\sum_i j_i} \times 100\% ;$$

- Low over-potential (this determines the energy efficiency of the process, defined as

$$\varepsilon_{\text{energy}} = \frac{\sum_i (E_{\text{anode},i}^0 - E_{\text{cathode},i}^0) \times \varepsilon_{\text{Faradaic},i}}{V_{\text{cell}}} \times 100\% ;$$

where E_{anode}^0 and E_{cathode}^0 are the standard redox potentials of the anode and cathode reactions, respectively, and V_{cell} is the measured cell voltage; and

- High conversion efficiency (this gives the ratio of the converted CO₂ versus the CO₂ feed) defined as

$$\varepsilon_{\text{conversion}} = \frac{\dot{n}_{\text{CO}_2, \text{converted}}}{\dot{n}_{\text{CO}_2, \text{in}}} \times 100\% .$$

If an electrolyzer cell does not fulfil any of these points, it cannot be competitive on a practical scale with other non-electrochemical technologies.

Hence, there would also be a need for a novel CO₂ electrolyzer cell and process, in the case of which the cell architecture and the operational parameters are optimized in order to fulfil the above goals.

Furthermore, there would be also a need for providing, especially for industrial applications, a large-sized and stack-based modular CO₂ electrolyzer cell, i.e. a multi-stack electrolyzer cell that consists of more than one, preferably several electrolyzer stacks, wherein said stacks can be manufactured relatively simply and inexpensively.

In most cases, industrial CO₂-sources provide gaseous CO₂ at elevated pressures. Moreover, industrial processes making use of various gas-phase carbon-based substances, such as e.g. syngas, carbon monoxide, methane, ethane, ethylene, etc., as feedstocks for producing other products require the feedstocks also at elevated pressures; here, and in
5 what follows, the term 'elevated pressure' refers to differential pressure values falling into the range of about 0 bar to at most about 30 bar.

In light of this, there would be a clear need for a CO₂ electrolyzer cell that withstands elevated pressures, especially at its cathodic side.

A yet further object of the present invention is to provide a CO₂ electrolyzer cell
10 that can be easily and simply restructured according to needs if a change in the required production rate or even in the type of product arises.

Additional objects, as well as aspects, features and advantages, of the present invention will be set forth in the description which follows.

Summary of the invention

15 The above goals are achieved by a continuous-flow multi-stack electrolyzer cell according to claim 1. Further preferred embodiments of the cell according to the invention are set forth in claims 2 to 12. The above objects are furthermore achieved by a CO₂ electrolyzer setup according to claim 13 to convert starting gaseous carbon dioxide to final gas-phase product(s). Preferred embodiments of the CO₂ electrolyzer according to the
20 invention are defined by claims 14 to 21. The above objects are also achieved by a method to convert gaseous carbon dioxide, CO₂, to at least one gas-phase product in accordance with claim 22.

In particular, the invention relates to new components and a new assembly of a carbon dioxide electrolyzer cell capable of operating at elevated differential pressures with
25 high conversion rates. It is based on the electrochemical reduction of gaseous carbon dioxide to gas-phase products (see table 1 below) and an oxidation reaction (e.g., that of water, $\text{H}_2\text{O} - 2\text{e}^- = 2\text{H}^+ + 0.5 \text{O}_2$) at the cathode and anode sides, respectively; the carbon dioxide used is preferentially humidified before its feeding into the electrolyzer cell.

Table. 1. A few possible reactions resulting in gas-phase products in CO₂ electrolysis.

Product	Reaction	Standard reduction potential (V vs. standard hydrogen electrode, at pH=7)
carbon monoxide	$\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- = \text{CO} + 2\text{OH}^-$	-0.51
<i>Hydrocarbons</i>		
methane	$\text{CO}_2 + 6\text{H}_2\text{O} + 8\text{e}^- = \text{CH}_4 + 8\text{OH}^-$	-0.24
ethane	$2\text{CO}_2 + 10\text{H}_2\text{O} + 14\text{e}^- = \text{C}_2\text{H}_6 + 14\text{OH}^-$	-0.27
ethylene	$2\text{CO}_2 + 8\text{H}_2\text{O} + 12\text{e}^- = \text{C}_2\text{H}_4 + 12\text{OH}^-$	-0.34
<i>Side reaction</i>		
hydrogen	$2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2 + 2\text{OH}^-$	-0.42

Due to the proposed technological novelties and the modular construction, the presented electrolyzer cell architecture is highly scalable and flexible. The cell can be easily scaled, both in terms of its size/dimensions and the number of stacks made use of, while maintaining pressure tolerance. Thus, based on the novel concept of multi-stack configuration in the field of CO₂ electrolysis, a CO₂ electrolyzer cell is built, in which the number of stacks is up to even ten or more, ranges preferably from two to seven, more preferably from three to six, and most preferably it is three, or four, or five, or six.

Furthermore, the cell architecture allows to couple the individual electrolyzer stacks either in parallel or in series, or in a mixed way in terms of gas management. Surprisingly, it was found that by changing only one element of the electrolyzer cell (and rearranging others), the operation can be switched from series to parallel. Thus, the cell can be operated to achieve either extraordinary high conversion rate or conversion efficiency, upon the needs. The employed catalysts, gas diffusion layers and ion exchange membranes allow flexibility in generating different gas-phase products. This allows the application of the CO₂ electrolyzer cell according to the invention in various industries, such as the chemical, oil, and energy industry. It is to be noted that the present invention is not limited to CO₂ electrolyzer cells only, upon appropriate routine modifications, it can be applied to other electrochemical setups (e.g., N₂-reduction cells for ammonia production) as well.

In the present invention, several stacks (electrocatalyst layers and membranes) are connected in series (electrically), confined by bipolar plate assemblies, functioning as anode of one stack on one side and as cathode for the subsequent stack on the other side (similar to PEM fuel cells or water electrolyzers).

5 The specific multi-stack cell architecture is realized by the application of two-component bipolar plate assemblies in forming said individual electrolyzer stacks. Here, a first component of a certain bipolar plate assembly forms the anodic part of the stack, while the second component of said bipolar plate assembly forms the cathodic part of a stack arranged next to said stack. In this way, a series of electrolyzer stacks can be formed,
10 wherein some flow structure elements of the cathodic/anodic flow paths within the cell, i.e. cavities and channels for the gaseous flow on the cathodic part, as well as cavities and channels for the liquid flow on the anodic part of the cell, are prepared on/in and between the opposite side surfaces of the first and second components of the bipolar plate assemblies.

15 Furthermore, the serial/parallel flow-channel configuration is achieved by selectively forming ring shaped spacer elements, i.e. the anode side distances, which practically support subsequent bipolar plate assemblies in the electrolyzer cell when the cell is assembled, with through channels; in particular, in harmony with the modular construction, two different kinds of spacer elements are provided, a first type with a single
20 internal gas transport channel in the peripheral portion of the spacer element, and a second type with two gas transport channels located diametrically opposite to one another in the peripheral portion of the spacer element. When assembling the electrolyzer cell, making use of the first type spacer element between subsequent bipolar plate assemblies allows the formation of a continuous gas flow path within the cell (that is, the individual stacks are
25 connected in series in terms of the cell's gas management), while making use of the second type spacer element between subsequent bipolar plate assemblies results in the formation of a gas flow path with parallel sections within the cell (that is, the stack gas flow paths in each of the individual stacks are connected in parallel in terms of the cell's gas management). The use of said specific spacer elements also allows of establishing a
30 structured gas flow path within the multi-stack electrolyzer cell which can equally contain serial sections and parallel sections.

That is, the function of the bipolar plate assemblies and the end units is complex: (i) they form the current collectors which are in contact with the catalyst layers, (ii) as the reactants are fed to the catalyst layer through the channels formed in these plates, they are responsible for the reactants supply to the cell active area, and for the proper outlet of the products (iii) these contribute to the mechanical strength of the cell. Furthermore, they play a significant role in the heat management of the electrolyzer cell, too. To serve this purpose, a system of in-plane flow-channels are formed on each of said elements in a surface thereof to increase the surface area and to help the transport processes. Said flow-channels are organized into various flow-field designs of specific geometry that are specifically optimized for the first time.

A further component made use of in the CO₂ electrolyzer cell according to the invention is a custom designed and assembled anode side structural element made of titan (Ti) frit (Ti-frit). Said Ti-frit is made of Ti powder of different average particle size. Ti-frit is actually manufactured by pressing the Ti-particles. The anode catalyst is deposited either directly on this Ti-frit through e.g. wet-chemical synthesis, or is synthesized separately and immobilized subsequently on the Ti-frit.

As for the cathode catalyst applied in the CO₂ electrolyzer cell according to the invention, it is immobilized on a high surface area carbon support (i.e. the GDL), which is in direct contact of the bipolar plate assembly. CO₂ gas is fed to the catalyst through this GDL. At the same time, the catalyst is in direct contact with the PEM, which allows facile ion transport.

A yet further component employed within the CO₂ electrolyzer cell according to the invention is a pressure chamber formed within specific end units arranged at both, i.e. the cathode-side and the anode-side ends of the cell. Said pressure chambers provide adaptive pressure control on the stacks from both sides, thus providing uniform pressure distribution throughout the stacks. This construction inhibits deformation of the cell body, and thus avoids the decrease in the contact area between the internal components. This results in a stable cell resistance even at elevated pressures. Importantly, the application of the end units eliminates the requisite of moving parts (such as pistons or valves) or elastic plastic elements as pressure controlling means within the cell. Furthermore, unlike any external pressure control, the employment of pressure chambers in said end units is

inherently safe, because the pressure in the pressure chambers can never be higher than the pressure generated in the electrolyzer stacks. To ensure pressure independent electrochemical performance, the pressure chambers are applied in pairs, i.e. one at the cathode-side and another one at the anode-side of the electrolyzer cell according to the invention.

Brief description of the drawings

In what follows, the invention is described in detail with reference to the accompanying drawings, wherein

- Figure 1 illustrates simplified operation of a carbon dioxide electrolyzer setup according to the invention fed with (humidified) CO₂ gas on the cathode side and with tempered anolyte on the anode side of the electrolyzer cell used therein;
- Figure 2A is a schematic cross-sectional representation of a single-stack electrolyzer cell usable in the carbon dioxide electrolyzer setup shown in Figure 1;
- Figure 2B is an expanded view of a part of the stack exemplified in Figure 2A;
- Figures 3A and 3B are complete upper and lower, respectively, perspective views of a specific exemplary embodiment of an electrolyzer cell according to the invention with three stacks used to convert carbon dioxide gas to various gas-phase products;
- Figure 4 is a partially exploded view of a multi-stack electrolyzer cell according to the invention comprising n stacks with one electrolyzer stack exploded;
- Figure 5 is a bottom view of a preferred two-component bipolar plate assembly used as the first (anodic) component of an intermediate electrolyzer stack (stack $i+1$) of the cell, as well as the second (cathodic) part of an adjacent intermediate electrolyzer stack (stack i) of the cell (here, $0 < i < n-1$, i, n are integer numbers);
- Figure 5A is a cross-sectional view of the bipolar plate assembly illustrated in Figure 5 along the A-A section;
- Figure 5B is a cross-sectional view of the bipolar plate assembly illustrated in Figure 5 along the B-B section;
- Figure 6 is a cross-sectional view of a 3-stack cell along the A-A section shown in Figure 3A assembled to accomplish a parallel flow configuration in terms of CO₂ supply of the cell; here, the system of flow-channels and cavities shown in grey

represents the way of gas flow within the cell from the CO₂ inlet to the CO₂ and product outlet;

- Figure 7 is a cross-sectional view of the 3-stack cell along the A-A section shown in Figure 3A assembled to accomplish a serial configuration in terms of CO₂ supply of the cell; here, the system of flow-channels and cavities shown in grey represents the way of gas flow within the cell from the CO₂ inlet to the CO₂ and product outlet;
- Figure 8 is a cross-sectional view of the 3-stack cell along the B-B section shown in Figure 3A in the serial/parallel configuration; here, the system of flow-channels and cavities shown in grey represents the way of fluid (i.e. anolyte) flow within the cell from the anolyte inlet to the anolyte and anodic product (in particular O₂ when water is used as anolyte) outlet;
- Figure 9 illustrates various flow patterns formed in the surface of the cathode current collector used in the electrolyzer cell according to the present invention; here Figures 9(a) to (c) show some exemplary designs with CO₂ fed into the stack at the centre and CO₂ collection from the stack along an outer peripheral ring, while Figure (d) shows a further exemplary design with CO₂ fed into the stack on the perimeter of the cathode current collector and CO₂ collection from the stack also on the perimeter of the cathode current collector, but at a position located opposite relative to the point where CO₂ is introduced, after passing over a double spiral pattern;
- Figure 10A illustrates a possible preferred embodiment of the anode-side spacer element used to accomplish a serial gas flow configuration between two adjacent stacks/bipolar plate assemblies in a multi-stack electrolyzer cell upon assemblage;
- Figure 10B illustrates a possible preferred embodiment of the anode-side spacer element used to accomplish a parallel gas flow configuration between two adjacent stacks/bipolar plate assemblies in a multi-stack electrolyzer cell upon assemblage;
- Figures 11A and 11B show a possible preferred embodiment of the anode current collector, that is, the anodic part of the bipolar plate assembly in Figure 5, in top and bottom views, respectively, formed with a flow pattern in one of its side surfaces, highlighting the cavities formed for O-ring sealings;
- Figures 12A and 12B are exploded views of a single stack in a multi-stack electrolyzer cell assembled with serial or parallel gas flow configurations, respectively;

- Figure 13 illustrates the effects of the increase in the number of individual electrolyzer stacks applied in the electrolyzer cell according to the present invention assembled in either a serial or a parallel gas flow configuration; in particular, in plot (a), the CO₂ conversions during electrolysis at $\Delta U = -2.75$ V/stack achievable with a 1-stack and a 3-stack serial connected electrolyzer at different CO₂ feed rates are plotted, and in plot (b), the CO₂ conversion during electrolysis at different cell voltages achievable with an electrolyzer cell consisting of one stack or three stacks, connected in parallel (with identical stack normalized gas feed), are shown;
- Figure 14 shows current density versus operational stack-voltage of a 3-stack CO₂ electrolyzer cell according to the invention used for syngas (H₂/CO mixture on Ag catalyst) or hydrocarbon (CH₄ and C₂H₄ on Cu catalyst) formation, recorded by linear sweep voltammetry (LSV) at $v = 10$ mV s⁻¹ sweep rate with different catalyst containing cathode gas diffusion electrodes (GDEs);
- Figure 15 is a chronoamperometric curve taken at $\Delta U = -3$ V/stack for a 3-stack CO₂ electrolyzer cell according to the present invention, using a 1 mg cm⁻² Ag containing cathode GDE, immobilized on Sigracet39BC carbon paper by spray coating;
- Figure 16 presents gas chromatograms recorded during a chronoamperometric measurement at $\Delta U = -2.75$ V/stack performed with a 3-stack CO₂ electrolyzer cell according to the present invention, using Ag catalyst [plot (a)] or Cu catalysts [plot (b)];
- Figure 17 shows partial current densities for CO and H₂ formation (ordinates to the left), as well as the ratio of the partial current densities (ordinates to the right) at different cell voltages (obtained by chronoamperometric and gas chromatography measurements);
- Figure 18 shows partial current densities for H₂ and CO formation (ordinates to the left) and CO₂ conversion (ordinates to the right) during electrolysis at $\Delta U = -2.75$ V as a function of the Ag catalyst amount in the cathode GDE;
- Figure 19 shows partial current densities for H₂ and CO formation (ordinates to the left) and CO₂ conversion (ordinates to the right) during electrolysis at $\Delta U = -2.75$ V as a function of the applied cathode spacing;
- Figure 20 presents partial current densities for H₂ and CO formation (ordinates to the left) and CO₂ conversion (ordinates to the right) during electrolysis at $\Delta U = -2.75$ V as

- a function of the depth of the flow-pattern applied in the cathodic side of the electrolyzer cell according to the invention;
- Figure 21 illustrates partial current densities for H₂ and CO formation (ordinates to the left) and CO₂ conversion (ordinates to the right) during electrolysis at $\Delta U = -2.75$ V as a function of carbon-dioxide flow rate (normalized with the surface area) in the cathode compartment of the electrolyzer cell according to the invention;
 - Figure 22 shows partial current densities for H₂ and CO formation (ordinates to the left) and CO₂ conversion (ordinates to the right) during electrolysis at $\Delta U = -2.75$ V as a function of the anolyte (1M KOH) temperature (at $\sim 9 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$ feed rate) taking place in the electrolyzer cell according to the invention;
 - Figure 23 presents LSV curves recorded at $v = 10 \text{ mV s}^{-1}$ sweep rate under various differential CO₂ pressures during electrolysis performed in the electrolyzer cell according to the invention; and
 - Figure 24 shows current densities at different cell voltages (plot A) and the ratio of the partial current densities (plot B) during electrolysis at $\Delta U = -2.75$ V, both as a function of the differential CO₂ pressure.

Description of possible embodiments

Figure 1 illustrates an exemplary embodiment of a CO₂ electrolyzer setup 200 comprising a CO₂ electrolyzer (electrochemical) cell 100 used to generate gaseous products at elevated pressures with high conversion rates via the electrolysis of gaseous CO₂ fed into the cell 100 which comprises a cathode 101 on a cathodic side, an anode 103 on an anodic side and a separator 102 to separate said cathode 101 and anode 102 from one another; here, the separator 102 is preferably a PEM element (e.g., an anion exchange membrane or a cation exchange membrane or a bipolar membrane). Said cell 100 is equipped with at least one gas inlet 101a and at least one gas outlet 101b, both being in gas connection with the cathodic side of the cell 100. Said cell 100 is also equipped with at least one fluid inlet 103a and at least one fluid outlet 103b, both being in fluid connection with the anodic side of the cell 100. The setup 200 further comprises a source 201 of gaseous CO₂, a humidifier 203 to humidify the gaseous CO₂, a power supply 220 to energize the electrochemical cell 100, an anolyte refresher unit 211 to regenerate an anolyte 213 used in the anodic side of the cell 100, a water separator 208 to remove

moisture from the gaseous product(s) produced via the electrolysis of gaseous CO₂ in the cathodic side of the cell 100, a back pressure regulator 209 to pressurize the cell 100 to maintain an elevated pressure (up to 30 bars, preferably up to 20 bars) within the cell 100, as well as a gaseous product outlet 216 that opens into a gas-phase product receptacle (not illustrated). As the CO₂ source 201, either a source of pure gaseous CO₂ or a source that supplies CO₂ in the form of a gas mixture, can be used. Optionally, the setup 200 further comprises any of a mass flow controller 202 to accurately control the mass flow of the gaseous CO₂ fed into the cathodic side of the cell 100 and appropriate pressure gauges 210, 210' to characterize the pressure prevailing within the cell 100. The CO₂ source 201 is connected to the gas inlet 101a of the cell 100 via an appropriate pipe 204, while the product outlet 216 is connected to the gas outlet 101b of the cell 100 via a further pipe 207. As a result, a continuous flow-path forms from said CO₂ source 201 to the product outlet 216 through the cathodic side of the cell 100. The mass flow controller 202 is preferably inserted into the pipe 204 downstream of the CO₂ source 201. The humidifier 203 is preferably inserted into the pipe 204 downstream of the mass flow controller 202, to humidify the gaseous CO₂ before its entry into the cell 100. The humidifier 203 is preferably a temperature-controlled bubbling type humidifier, however, any other kind of humidifier can also be applied here. Optionally, the pressure gauge 210 is also inserted into the pipe 204 to continuously monitor the inlet pressure in the cell 100. The water separator 208 is inserted into the pipe 207 downstream of the cell 100. The back pressure regulator 209 is inserted into the pipe 207 downstream of said water separator 208. As the water separator 208 and the back pressure regulator 209 any kind of water separator and pressure regulator can be used, as is clear for a skilled person in the art. Optionally, the further pressure gauge 210' is inserted into the pipe 207 between the cell 100 and the back pressure regulator 209 to continuously monitor the outlet pressure in the cell 100. Thus, by means of the pressure gauges 210, 210', the pressure drop through the cell 100 can also be determined.

The anodic side of the cell 100 is in fluid connection through its fluid outlet 103b and a pipe 205 with an inlet port 211a of the anolyte refresher unit 211. Furthermore, the anodic side of the cell 100 is in fluid connection through its fluid inlet 103a and a pipe 206 with an outlet port 211b of the anolyte refresher unit 211. Thus, a closed continuous flow-path forms on the anodic side of the cell 100 between said anodic side and the anolyte

refresher unit 211. Through this closed flow-path, an anolyte 213 is circulated by means of a pump 215 inserted preferably into the pipe 206 between the anodic side, through an appropriate system of fluidic channels formed in the anode, and the refresher unit 211 to refresh spoilt anolyte (if needed) taking place in electrochemical reaction(s) at the anodic side in the cell 100. Furthermore, to provide the possibility of venting in said anolyte refresher unit 211, said unit is also equipped with venting means 214 through which surplus gas accumulating in the refresher unit 211 separated from spoilt anolyte 213 during the process of refreshment of the anolyte 213 can leave the unit. For the optimal operation of the CO₂ electrolyzer setup 200, and in turn the cell 100 as well, the anolyte refresher unit 211 is in thermal coupling with appropriate tempering means 212 to adjust the temperature of the anolyte 213, that is to cool/heat it. To this end, as is clear for a skilled person in the art, any kind of tempering means, that is, cooler/heater means can be used.

As far as the electric power supply of the cell 100 is concerned, a negative pole of said power supply 220 is electrically connected with the cathodic side of the cell 100, in particular a cathode-side contact plate, while a positive pole of said power supply 220 is electrically connected with the anodic side of the cell 100, in particular an anode-side contact plate (to be discussed later in detail). Said power supply 220 can be either the grid itself or any local source of electricity, i.e. a solar, wind, nuclear one. A battery, either a disposable or a secondary one, can be equally used as the power supply 220.

In operation, the carbon dioxide (either pure, or a gas mixture) is first humidified at a controlled temperature (which is preferentially in the range of about 20°C to about 70°C), and then fed to the cathodic side of the cell 100. Here, there is no solution feed to the cathode. When feeding only humidified CO₂ gas to the cathodic side, the reactant concentration remains very high on the catalyst, and therefore high reaction rates (currents) can be achieved. Furthermore, because the lack of solution feed, no reactant is washed out unreacted with this stream. As the type of reactant has an important and complex effect on cell performance, this modification regarding the type of feed represents a significant difference in comparison with most prior art solutions. In the presented CO₂ electrolyzer setup 200, only gas phase products form in the electrolysis reactions that take place in the cell 100. Depending on the catalysts used in the cell 100 and the applied CO₂ electrolysis reactions (see Table 1) various products are obtained; as examples (i) syngas (CO/H₂

mixture with controlled composition) and (ii) ethylene are mentioned here. The gaseous products forming in the cathodic part, that is, within the system of flow-channels fabricated in cathode-side constructional elements (discussed later), leave the cell 100 and then are introduced into the water separator 208 to remove moisture. The anolyte 213 (employed as
5 aqueous solution, the type of which depends on the type of separator 102 used, i.e. the applied ion-exchange membrane) is directly and continuously fed into the anodic side of the cell 100 with the pump 215. Said anolyte 213 then flows through the cell 100 in a system of flow-channels fabricated in anode-side constructional elements and collects gaseous oxygen that forms in the electrolysis reaction of CO₂ along its path. When the
10 stream of anolyte 213 leaves the cell 100, and before being recirculated into said cell 100, the oxygen content in said anolyte 213 gets released within the anolyte refresher unit 211 and then is vented out through said venting means 214. Notably, other value-added anode processes (other than water oxidation, e.g. chlorine formation or alcohol oxidation) can be coupled to CO₂ conversion, as is clear for a skilled person in the art; the architecture of
15 said setup 200/cell 100 is not confined to water oxidation at all. Furthermore, during operation of the setup 200, the pressure in the cell 100 is continuously controlled by the back pressure regulator 209. Thus, contrary to most prior art solutions, the electrolyzer cell 100 actually works under continuous differential pressure.

Figure 2A is the schematic cross-sectional view of a single exemplary PEM
20 electrolyzer stack that can be used in the CO₂ electrolyzer cell 100/setup 200 shown in Figure 1; Figure 2B is an expanded view of a part of the stack taken in the vicinity of the b-b line shown in Figure 2A. Said stack comprises a PEM, in particular an ion-exchange membrane 7, 102, held in place by (i.e. cathode- and anode-side) spacer elements 9(a, b) arranged at opposite sides of said membrane 7 along its peripheral edge portion. The
25 membrane 7 functions as a separator element, it separates the cathode 101 and the anode 103 (i.e. the cathodic and anodic sides) of the stack from one another. At the cathodic side, there is a layer of (cathode) catalyst 6b arranged adjacent to and in direct contact with the membrane 7. On the layer of the catalyst 6b, on a surface thereof facing away the membrane 7, a gas diffusion layer 6a is arranged in direct contact with said layer of
30 catalyst 6b. On this gas diffusion layer 6a, a plate of a cathode current collector 5 is arranged in direct contact with said gas diffusion layer 6a.

Here, the membrane 7 is an anion exchange membrane, available under the tradenames of e.g. Fumasep, Selemion and Sustanion, just to mention a couple of examples only, which allows, in operation, the migration of hydroxide ions (OH^- ions; charges, and thus current) between the cathodic and anodic sides of the stack through its bulk, while
5 water (H_2O) diffusing through it from the anodic to the cathodic side takes part in the electrolytic reduction of CO_2 at the cathodic side. As in this case no electrons are transported through the membrane 7, said membrane 7 actually acts as a layer of electrical insulation between the cathodic and anodic sides of the stack. As is clear for a skilled person in the art, depending on the electrolytic reaction to be performed at the cathodic
10 side, cation exchange membranes, available under the tradenames of e.g. Nafion and Aquivion, or further bipolar membranes (e.g. Fumasep FBM) can equally be employed as the membrane 7.

The cathode current collector 5, on the one hand, acts as a current distributing element, that is, it evenly distributes the electric current received from an external power
15 supply through a cathode-side contact plate (discussed below) over the cathode-side gas diffusion layer 6a and, on the other hand, provides appropriate space for the compression of said cathode-side gas diffusion layer 6a. The cathode current collector 5 comprises a system of in-plane flow-channels 5'' of height M formed on/in a surface of the cathode current collector 5 that faces towards the membrane 7; said system of flow-channels 5''
20 corresponds to various geometrical patterns (see e.g. Figure 9). The patterned formation of the flow-channels 5'' allows an even distribution of the gaseous CO_2 over the cathode-side gas diffusion layer 6a. The cathode current collector 5 is also provided with, in the form of throughout openings, an inlet for feeding gaseous CO_2 to the gas diffusion layer 6a and an outlet for discharging the gaseous product that forms at the cathodic side of the stack in the
25 electrolysis reaction (reduction) of CO_2 .

The cathode-side gas diffusion layer 6a allows, in operation, a CO_2 transport to the layer of cathode catalyst 6b in contact with the membrane 7 where reduction reaction of the gaseous CO_2 takes place and thus the desired product forms. The gas diffusion layer 6a also allows the transport of said gaseous product (in the form of a mixture also comprising
30 the amount of non-converted CO_2) along the cathodic flow-channel structure towards a CO_2 and product outlet of the stack. To provide effective transport properties, as the cathode-side gas diffusion layer 6a any of a carbon cloth, carbon felt and carbon film can

be used, preferably modified with a microporous layer, as is known by a skilled person in the art. As the cathode catalyst 6b, a plurality of catalysts can be used, the cathode catalysts applied in this case are preferably Ag/C and Cu/C catalysts. The gas diffusion layer 6a and the layer of cathode catalyst 6b have a total thickness H, as is shown in Figure 2B, that
5 represents cathode compartment spacing.

In turn, at the anodic side, there is a layer of anode catalyst 8b arranged adjacent to and in direct contact with the membrane 7; here, IrO_x , RuO_x , NiO_x , and TiO_x are highly preferred anode catalysts. On the layer of the anode catalyst 8b, on a surface thereof facing away the membrane 7, an anode-side gas diffusion layer 8a is arranged in direct contact
10 with said layer of anode catalyst 8b. Said anode-side gas diffusion layer 8a is formed of a layer of titan-frit (Ti-frit) in the form of pressed Ti powder of different average particle size (in the range of preferably 50-200 μm) or a layer nickel-frit (Ni-frit) in the form of pressed Ni powder of different average particle size (in the range of preferably 50-200 μm), titan-mesh (Ti-mesh) or nickel-mesh (Ni-mesh), both having a wire thickness and
15 pore size preferably in the range of 50-200 μm , just to mention a few examples. On the anode-side gas diffusion layer 8a, a plate of an anode current collector 10 is arranged in direct contact with said gas diffusion layer 8a. The anode current collector 10 also comprises a system of flow-channels 5' formed in a surface of the anode current collector 10 that faces towards the membrane 7.

20 The anode current collector 10, on the one hand, acts as a current distributing element, that is, it evenly distributes the electric current received from the external power supply through an anode-side contact plate (discussed below) over the anode-side gas diffusion layer 8a and, on the other hand, provides appropriate space for the compression of the anode-side gas diffusion layer 8a. The anode current collector 10 is also provided
25 with, in the form of through openings, an inlet for feeding liquid anolyte to the anode-side gas diffusion layer 8a and an outlet for discharging the mixture of liquid anolyte and anodic products (e.g. gaseous O_2 if the anolyte also contains water) appearing at the anodic side of the stack in the electrolysis reactions (oxidation) of the anolyte taking place at the anodic side.

30 As is clear for a skilled person in the art, the cathode-side gas diffusion layer 6a, the layer of cathode catalyst 6b, the membrane 7, the layer of anode catalyst 8b and the

anode-side gas diffusion layer 8a can be combined into a single unit, i.e. a membrane electrode assembly, and applied in the form of said assembly to construct a modular electrolyzer stack by arranging such a membrane electrode assembly between the cathode current collector 5 and the anode current collector 10 both in electrical contact and in gaseous/fluid communication therewith and positioning said assembly properly by the anode-side spacer elements 9a, 9b. It should be here also noted that the electrolyzer stack obtained in this way and shown in Figure 2 is essentially a zero-gap electrolyzer stack and, as discussed below, can also be used to construct multi-stack CO₂ electrolyzer cells 100'' of modular structure.

Figures 3 and 4 illustrate exemplary multi-stack electrolyzer cells 100', 100'' with more than one electrolyzer stack modules. In particular, Figures 3A and 3B are the upper and lower, respectively, perspective views of an electrolyzer cell 100' comprising three electrolyzer stacks used to convert gaseous CO₂ to gaseous products at elevated pressures and with high conversion rates via electrolysis. Figure 4 is a partially exploded view of a multi-stack electrolyzer cell 100'' according to the invention which comprises n stacks 40 (n is a positive integer) with one electrolyzer stack exploded in the series of stacks 40. According to practical considerations, however, one chooses the number n to range from at least one to even ten or more; in particular, the number n of the applied stacks is preferably between two and seven, more preferably between three and six, and most preferably it is three, or four, or five, or six in one electrolyzer cell 100''.

As can be seen in Figures 3A, 3B and 4, the electrolyzer cells 100', 100'' are of modular construction, the components used to construct the cells 100', 100'' are provided in the form of plate-like elements of different function. The plate-like components may be of arbitrary planar shape; in the exemplary embodiments illustrated in Figures 3A, 3B and 4, the components are essentially circular in shape. Furthermore, to assist fast assembling and/or reassembling of said components into the cells 100', 100'', each of the plate-like components is provided with an assemblage assisting recess 52 formed in the peripheral edge thereof. The assemblage assisting recesses 52 thus clearly show how to combine the components into a cell properly; at the correct arrangement/orientation of the components, said recesses 52 are aligned.

Upon assembling said components into a cell, the obtained cell contains the individual electrolyzer stacks side by side along a longitudinal direction. Here, and from now on, the term “longitudinal” refers to a direction that is essentially perpendicular to the surface planes of said plate-like components. Thus, as is shown in Figures 3A, 3B and 4, the plate-like components are provided with a plurality of through holes along said longitudinal direction. A part of said holes serves as bore holes 1a to receive screws 1 with shrink tubes and pads used to assemble said components into the cells 100', 100'' and then to connect said components in a sealed manner by means of screw-nuts 14 with pads screwed onto the screws 1 inserted into the respective bore holes 1a. The remaining part of the holes formed in said plate-like components, configured to be properly aligned with one another and sealed by means of specific channel sealing means (detailed below) that can be arranged around each of the holes and between the plate-like components, serves to form a longitudinal flow-through portion of the cathodic and anodic side transport channel structures within the cells 100', 100''. In particular, at the cathodic side, one of said holes serves as a gas inlet 21 to introduce gaseous CO₂ into the electrolyzer stacks 40 assembled either in serial or parallel (or in mixed) configuration in terms of CO₂ supply and transport within the cell, while another two of said holes serve (i) as a fluid inlet 23 to introduce a liquid anolyte into the electrolyzer stacks 40 assembled in serial/parallel configuration and (ii) as a fluid outlet 24 to discharge spoilt anolyte with gaseous anodic products (e.g. O₂) that form in the individual stacks 40 in the anode-side electrolysis reaction(s). In turn, at the anodic side, one of said holes serves as a gas outlet 22 to discharge non-reacted CO₂ fed in in surplus with gaseous cathodic products that form in the stacks 40 in the cathode-side electrolysis of CO₂.

Referring now to Figure 4, the multi-stack CO₂ electrolyzer cell 100'' according to the invention is used to decompose gaseous CO₂ by electrolysis and thus, depending on the applied catalysts and the anolyte, to generate various gaseous products. To this end, the cell 100'' comprises a certain number *n* of electrolyzer stacks 40 arranged adjacent to and in sealed fluid/gaseous communication with each other through the longitudinal portion of the cathodic and anodic side transport channel structures. Furthermore, said electrolyzer stacks 40 are coupled electrically with one another and the electrical terminals of the cell 100'', i.e. with the cathode-side and anode-side contact plates 4, 11 in series. Thus, the cell 100'' contains a series of electrolyzer stacks 40 consisting of interconnected intermediate

stacks sandwiched between a cathode-side end unit 26 and an anode-side end unit 27 arranged at opposite ends of said series along the longitudinal direction.

The cathode-side end unit 26 closes the series of electrolyzer stacks 40 at the cathodic side of the cell 100". An inner surface of the cathode-side end unit 26 is in direct
5 contact with the first stack 40 of said series, while an outer surface of the cathode-side end unit 26 is, in practice, exposed to the environment. The cathode-side end unit 26 is itself of a modular structure; it comprises a cathode-side contact plate 4 with the inner surface concerned, a cathode-side insulation 3 arranged on said cathode-side contact plate 4 and a cathode-side endplate 2 with said outer surface arranged on the cathode-side insulation 3.
10 The cathode-side endplate 2 is provided with openings that are in gaseous/fluid communication with the cathodic and/or anodic transport channel structures, respectively, of the cell 100" through respective openings formed in the insulation 3 and the contact plate 4 in proper alignment with the openings concerned, that is, the gas inlet 21 for CO₂ supply, the fluid inlet 23 for anolyte supply and the fluid outlet 24 for spoilt anolyte (and
15 anodic product) discharge. In the assembled state of the cell 100", the openings formed in the cathode-side end unit 26 in alignment with one another form continuous longitudinal sealed flow-channels, each of which opens into the respective opening of the first electrolyzer stack 40. Here, sealing is achieved by appropriately sized sealing elements, preferably in the form of O-rings 15, 16, 17 made of a corrosion resistant plastic material
20 (e.g. Viton®), arranged between the endplate 2 and the insulation 3, the insulation 3 and the contact plate 4, as well as the contact plate 4 and said first stack around the respective openings. The cathode-side endplate 2 serves as a mechanical strengthening element and to enhance pressure-tightness of the cell 100" by means of the through screws 1. The cathode-side insulation 3 serves as an electrical insulation between the endplate 2 and the
25 cathode-side contact plate 4. The cathode-side insulation 3 also accommodates a cathode-side pressure chamber that inhibits possible displacements of the inner components of the cell 100" towards the cathode-side endplate 2 when the cell 100" becomes pressurized upon starting its operation. Said pressure chamber is formed as a hollow cavity in the bulk of the cathode-side insulation 3 and extends over a given portion of the cathode-side
30 endplate 2 when the cell 100" is assembled. In such a case, the cathode-side pressure chamber is sealed by an O-ring 15 arranged in a circular groove around said cavity in the cathode-side insulation 3 between the insulation 3 and the endplate 2. Furthermore, the

cathode-side contact plate 4 serves as an electrical connection to an external electrical power source and simultaneously as a current distributing element that evenly distributes the electric current received from said power source through the inner surface of the cathode-side end unit 26 over the outermost surface of the very first stack in the series of intermediate stacks 40. The cathode-side contact plate 4 also helps with the feed-in of the gaseous CO₂ into the first electrolyzer stack 40 of the cell 100", and with the introduction and discharge of the liquid anolyte and the spoilt anolyte into and from, respectively, the first electrolyzer stack 40 of the cell 100".

The anode-side end unit 27 closes the series of electrolyzer stacks 40 at the anodic side of the cell 100". An inner surface of the anode-side end unit 27 is in direct contact with the last, i.e. the *n*-th, stack 40 of said series, while an outer surface of the anode-side end unit 27 is, in practice, exposed to the environment. The anode-side end unit 27 is itself of a modular structure; it comprises an anode-side contact plate 11 with the inner surface concerned, an anode-side insulation 12 arranged on said anode-side contact plate 11 and an anode-side endplate 13 with said outer surface arranged on the anode-side insulation 12. The anode-side endplate 13 is provided with an opening that is in gaseous communication with the cathodic transport channel structure of the cell 100" through respective openings formed in the anode-side insulation 12 and the anode-side contact plate 11 in proper alignment with the opening at issue, i.e. the gas outlet 22 for CO₂ and cathode product discharge. In the assembled state of the cell 100", the openings formed in the anode-side end unit 27 in alignment with one another form a continuous longitudinal sealed flow-channel that opens into the corresponding opening of the last electrolyzer stack 40. Here, sealing is achieved by appropriately sized sealing elements, preferably in the form of O-rings, arranged between said last stack and the anode-side contact plate 11, the anode-side contact plate 11 and the anode-side insulation 12, as well as the anode-side insulation 12 and the anode-side endplate 13 around the openings; the O-rings concerned are similar/equivalent with the O-rings employed in the cathode-side end unit 26. Here, the anode-side contact plate 11 serves as an electrical connection to an external electrical power source and simultaneously as a current distributing element that evenly distributes the electric current received from said power source through the inner surface of the anode-side end unit 27 over the outermost surface of the very last stack in the series of intermediate stacks 40. The anode-side contact plate 11 also helps with the discharge of

gaseous CO₂ mixed with the electrolysis product from the last electrolyzer stack 40 of the cell 100". The anode-side insulation 12 serves as an electrical insulation between the anode-side contact plate 11 and the anode-side endplate 13. The anode-side insulation 12 also accommodates an anode-side pressure chamber that inhibits possible displacements of the inner components of the cell 100" towards the anode-side endplate 13 when the cell 100" becomes pressurized upon starting its operation. Said pressure chamber is formed as a hollow cavity in the bulk of the anode-side insulation 12 and extends over a given portion of the anode-side endplate 13 when the cell 100" is assembled. In such a case, the anode-side pressure chamber is sealed by an O-ring 15 arranged in a circular groove around said cavity in the anode-side insulation 12 between the insulation 12 and the anode-side endplate 13. Furthermore, the anode-side endplate 13 serves as a mechanical strengthening element and to enhance pressure-tightness of the cell 100" by means of the screw-nuts 14 with pads screwed onto the screws 1 inserted through the entire structure of the cell 100" in the bore-holes 1a from the cathode-side endplate 2. In harmony with convention, the cathode-side contact plate 4 and the anode-side contact plate 11 are in electrical connections with the negative and positive, respectively, poles of the external power source.

Referring now to Figures 5, 5A and 5B, which illustrate the two-component bipolar plate assembly 40' in bottom view, in cross-sectional view taken along the A-A line and in cross-sectional view taken along the B-B line, respectively, the first component 40a of the assembly 40' (i.e. the anode current collector 10 in a single stack) and the second component 40b of the assembly 40' (i.e. the cathode current collector 5(a, b, c, d) in a single stack) are provided on their opposite side surfaces with certain elements of the cathodic and anodic side transport channel structures. In particular, the first component 40a is provided with entry/exit ports for the cathode-side and anode-side systems of flow-channels within the stack 40'. Said ports are: a stack inlet gas transport channel 41 and a stack outlet gas transport channel 42 for gas supply and transport (i.e. CO₂, desired product) at the cathodic side in the bipolar plate assembly 40', as well as a stack anolyte inlet channel 48, a stack anolyte outlet channel 49, a stack anolyte transport channel 43, and a stack anolyte and anodic product transport channel 44 for fluid supply and transport (i.e. anolyte; spoilt anolyte with anodic product, e.g. gaseous O₂) at the anodic side in the bipolar plate assembly 40'. The first component 40a is further provided with an in-plane

system of fluid flow-channels 5' of certain geometry on/in its side surface facing – when assembled into a cell – towards the cathode-side end unit. Said ports lead from said side surface to the opposite side surface of the first component 40b where each of said ports opens into a respective cavity which fully surrounds it, i.e. cavities 33a, 33b, 33c, 33d. Said
5 cavities and ports provide the fluid communication with respective longitudinal fluid flow-channels 41', 42', 43', 44' formed in the second component 40b. Said second component 40b is also provided with a stack gas inlet channel 46 and a stack gas outlet channel 47 for gas supply and transport (i.e. CO₂, desired product) at the cathodic side in the bipolar plate assembly 40', as well as an in-plane system of gas flow-channels 5'' of certain geometry
10 (see Figure 9). Said cavities are equipped with appropriate sealing members, in particular O-rings 16, 17, 17', 19 made of a corrosion resistant plastic material (e.g. Viton®) to seal the flow-channels when the cell is assembled and maintain pressure prevailing within the cell in operation.

The first and second components 40a, 40b of the assembly 40' are made of the
15 same electrically conducting compound as the other parts of the cell, which are responsible for conducting electricity, e.g. titanium, stainless steel, different alloys and composite materials. The ports and the cavities are formed by machining, in particular CNC-milling.

As is apparent from Figure 4, after assembling the CO₂ electrolyzer cell 100'' according to the invention, the cathode-side and the anode-side end units 26, 27 sandwich
20 *n* pieces of practically identical intermediate electrolyzer stacks 40, wherein the electrolyzer stacks 40 are coupled to each other (i) in series in terms of the power (electric current) management of the cell 100'', (ii) in parallel in terms of the anolyte supply and transport within the cell 100'', and (iii) in series or parallel, or in a mixed way in terms of CO₂ supply and transport within the cell 100''. Each stack 40 is constructed from the two-
25 component bipolar membrane assemblies 40' (see Figures 5A and 5B). In particular, each stack 40 comprises the first (anodic) component 40a of the *i*-th bipolar membrane assembly 40', the second (cathodic) component 40b of the adjacent, i.e. (*i*-1)-th bipolar membrane assembly 40' (here, $1 < i < n$, integer), a membrane electrode assembly discussed previously arranged between said first and second components 40a, 40b, and an
30 anode-side spacer element 9a, 9b inserted between said first and second components 40a, 40b of the bipolar membrane assembly 40' in the peripheral region thereof. Feature (i) is a consequence of the electric contact between subsequent stacks 40 in the cell 100''. Feature

(ii) is a consequence of the physical construction, i.e. the number of longitudinal channels provided in the anode-side spacer elements 9a, 9b for gas transport at the cathodic side and the orientation in which a certain spacer element 9a, 9b is actually arranged in the cell 100". In particular, as shown in Figure 10A, a single longitudinal channel 36 is provided in the spacer elements 9a to be used when connecting two adjacent stacks so as to form a serial gas flow-channel at the cathodic side of the cell 100"; the respective configuration of the stack is illustrated in exploded view in Figure 12A. Moreover, as shown in Figure 10B, two longitudinal channels 36 are provided in the spacer element 9b to be used when connecting two adjacent stacks so as to form gas flow-channels extending in parallel at the cathodic side of the cell 100"; here the longitudinal channels 36 are formed at diametrically opposite locations of the spacer element 9b. The respective configuration of the stack is illustrated in exploded view in Figure 12B.

In what follows, the cathode-side gas management and the anode-side fluid management is explained in more detail for a preferred embodiment of the multi-stack electrolyzer cell 100" comprising three individual stacks 40 or bipolar plate assemblies 40'. In particular, Figure 6 shows the 3-stack electrolyzer cell 100' in cross-sectional view taken along the A-A line illustrated in Figure 3A with a cell's gas flow path shown in grey; here, the cell 100' is assembled in parallel configuration of the stack gas flow paths of the individual stacks 40 in terms of CO₂ supply and transport within the cell 100'. Furthermore, Figure 7 illustrates the 3-stack electrolyzer cell 100' in cross-sectional view taken along the A-A line shown in Figure 3A with the cell's gas flow path shown again in grey; here, the cell 100' is assembled in serial configuration of the stack gas flow paths of the individual stacks 40 in terms of CO₂ supply and transport within the cell 100'. Yet further, Figure 8 shows the 3-stack electrolyzer cell 100' in cross-sectional view taken along the B-B line illustrated in Figure 3A with the cell's fluid flow path shown in grey; here, the cell 100' is assembled in any of the serial and parallel configurations of the individual stacks 40 in terms of CO₂ supply and transport within the cell 100', the stack fluid flow paths are combined to form a cell's fluid flow path in a parallel configuration in terms of anolyte supply and transport within the cell 100'.

Figure 6 illustrates a continuous cell's gas flow path that extends from the gas inlet 21 to the gas outlet 22 through a cathode-side pressure chamber 31 formed within the cathode-side end unit, in particular in the cathode side insulation 3, then through bores

formed in the cathode-side insulation 3 and the cathode-side contact plate 4 that open into a stack gas inlet 46 formed in the cathode current collector, then through said stack gas inlet 46 into grooves 45 of the flow pattern 5" (see Figure 9) formed in the a surface of the cathode current collector facing to the cathode-side gas-diffusion layer and thus into the first electrolyzer stack 40 arranged in the series of stacks (40) applied. The cell's gas flow path then extends further as an in-plane stack gas flow path of the first stack 40 formed between the cathode-side current collector and the cathode-side gas-diffusion layer being in partial contact with each other, and leaves the first stack 40 through a stack gas outlet 47 which is in gaseous communication with a sealed cavity 33b; said cavity 33b is formed in a surface of the anode current collector. The cell's gas flow path then extends from said cavity 33b through an outlet gas transport channel 35, then through bores formed in the anode-side contact plate 11 and the anode-side insulation 12 into an anode-side pressure chamber 32 formed within the anode-side end unit, in particular in the anode-side insulation 12, then from said anode-side pressure chamber 32 to the gas outlet 22. Here, the outlet gas transport channel 35 is formed by the stack outlet gas transport channels 42" (see Figure 9) formed in the cathode current collector, the internal gas transport channel 36 of the anode spacer element 9b (see Figure 10B) and the stack outlet gas transport channel 42 formed in the anode current collector (see e.g. Figure 11A).

Furthermore, to supply CO₂ into the second and the any subsequent stacks 40 too, the cell's flow path extends from the cathode-side pressure chamber 31 through an inlet gas transport channel 34 into sealed cavities 33a formed in said surface of the anode current collector of the individual stacks 40, wherein each of the cavities 33a is connected with the stack gas inlet 46 of the stack 40. Thus, in operation, all the stacks 40 are in gaseous communication with said inlet gas transport channel 34 which means a parallel gas transport configuration of the electrolyzer cell 100'. The inlet gas transport channel 34, which is formed by a stack inlet gas transport channel 41 formed in the cathode current collector, a further internal gas transport channel 36 of the anode spacer element 9b and a stack inlet gas channel 41, ends in an inlet gas transport channel end 34a, i.e. it is a dead furrow.

Figure 7 illustrates a continuous cell's gas flow path that extends from the gas inlet 21 to the gas outlet 22. Here, when the multi-stack electrolyzer cell 100' is assembled, due to (i) the employment of an anode spacer member 9a that has only a single internal gas

transport channel 36 (instead of two), and (ii) the fact that said anode spacer member 9a is arranged in the adjacent stacks with an orientation that is rotated with just 180° about an axis perpendicular to the spacer element 9a at the centre thereof, the cell's flow path becomes a flow path of the stack flow paths connected in series as a consequence of segmentation of the inlet gas transport channel 34 and the outlet gas transport channel 35 (see Figure 6).

Figure 8 illustrates a continuous cell's fluid flow path that extends from the fluid inlet 23 to the fluid outlet 24 through a continuous inlet flow transport channel formed by through channel 43' in the cathode current collector, through channel 38 in the spacer element and through channel 43 in the anode current collector of the electrolyzer stacks, then through sealed cavities 33c in flow communication with stack fluid inlets 48, then through the flow patterns 5' and through channels 49 into sealed cavities 33d, then from the cavities 33d in fluid communication with a continuous outlet flow transport channel formed by through channel 44 in the anode current collector, through channel 39 in the spacer element and through channel 44' in the cathode current collector of the electrolyzer stacks.

In what follows, the constructional components of a single electrolyzer stack 40, e.g. the one illustrated in Figure 4 as the exploded stack, constructed from two-component bipolar plate assemblies 40' are explained in more detail with reference to Figures 9 to 11.

In particular, Figure 9 shows four possible embodiments of the cathode current collector 5a, 5b, 5c, 5d (forming the second component 40b of the two-component bipolar plate assemblies used), wherein each embodiment is provided with a certain in-plane flow-channel structure or flow pattern 5''. The flow pattern 5'' is a crucial part in achieving homogeneous CO_2 feed to the cathodic side of the stacks and efficient product collection therefrom. Here, the CO_2 feed takes place through a stack gas inlet channel 46 extending longitudinally, while product collection is performed through a stack gas outlet channel 47 extending also along the longitudinal direction. Between said inlet and outlet channels 46 and 47, the gaseous CO_2 is transported and continuously involved the cathode electrolysis reaction and thus converts to the gaseous product within the grooves 45 of the continuous flow pattern 5'' which is in contact with the membrane electrode assembly (not illustrated). As it can be seen in Figure 9, in three exemplary flow designs, namely the flow designs of

Figures 5(a) to 5(c) corresponding to a labyrinth-type flow pattern, an offset circles-type flow pattern and a radial double spiral-type flow pattern, respectively, the gaseous CO₂ is fed at the centre, i.e. the stack gas inlet channel 46 is located at the centre of the cathode current collector, and collected all along an outer ring, i.e. the stack gas outlet channel 47 is arranged in the peripheral portion of the cathode current collector. Figure 5(d) illustrates such a further flow design, in the case of which the CO₂ is fed on the perimeter of the cathode current collector and collected at e.g. a diametrically opposite location of the cathode current collector after passing through a double-spiral pattern, that is, both the stack gas inlet and outlet channels 46, 47 are located in the peripheral region of the cathode current collector. Surprisingly, it was found that unlike in fuel cells, the best performing flow patterns were always those in which CO₂ was fed in the centre of the flow pattern.

It should be here noted that to use cathode current collectors 5a, 5b, 5c, 5d of different flow patterns 5'' together with the same anode current collector 10 in a multi-stack cell, or putting this another way, to use the second component 40b of various flow patterns 5'' of the two-component bipolar plate 40' with a single type first component 40a (i.e. provided with a unique flow pattern 5') thereof, the inlet gas transport channel 41 is formed specifically. In particular, the shape of said inlet gas transport channel 41 is circular at the side of the second component 40b with the flow pattern 5'', while it has a narrow elongated shape at the opposite side of the second component 40b to cover the stack gas inlet channel 46 independent of the fact whether it is formed at the centre or in a peripheral region of the second component 40b.

Figures 10A and 10B show possible embodiments of the anode-side spacer elements 9a, 9b to be arranged between the cathode current collector and the anode current collector in every electrolyzer stack 40 of the multi-stack electrolyzer cell 100', 100'' to accomplish either the serial or the parallel, respectively, cathode-side gas flow-channel configuration. The two kinds of anode-side spacer element 9a, 9b are practically identical, but the number of internal gas transport channels 36 extending in the longitudinal direction. With this unique choice of design, the anode-side spacer elements are such spacer elements that are configured to act as means for selectively choose the way two adjacent stack flow paths connect to one another in the gas flow path of the electrolyzer cell. The anode-side spacer elements 9a, 9b are made of electrical insulators, preferably

plastics or Teflon. Thus, said anode-side spacer elements 9a, 9b can be simply and cheaply fabricated, even on the industrial scale and in an automated manner.

Figure 11 presents the anode current collector 10 (which forms the first component 40a of the two-component bipolar plate assemblies) used in the CO₂ electrolyzer cells according to the invention, Figure 11A is a top view, while Figure 11B is a bottom view of the anode current collector 10, highlighting the cavities 33a, 33b, 33c, 33d provided for establishing a sealed gaseous/fluid communication for the gaseous/fluid management of the cell, as well as to accommodate the required sealing elements, i.e. the various O-rings.

Finally, Figures 12A and 12B illustrate a single stack 40 of a multi-stack electrolyzer cell assembled with serial and parallel cathode-side gas flow configurations, respectively, in exploded views. Figures 12A and 12B also show the advantage of the modular construction applied. In particular, by replacing the anode spacer element 9a having only a single internal gas transport channel 36 with an anode spacer element 9b comprising two internal gas transport channels 36, the flow configuration of the stack 40 concerned is simply modified from the serial one to the parallel one, and vice versa. That is, by simply disassembling the electrolyzer cell to stacks and then any of the stacks to components, replacing the anode spacer element(s) with anode spacer element(s) which is/are required for the desired cathode-side gas flow configuration, then reassembling each stacks from the components and then the cell from the stacks, a multi-stack electrolyzer cell of the desired gas flow management is obtained. Hence, the multi-stack electrolyzer cell according to the invention can be simply and rapidly matched with the operational needs, and practically on the spot.

In what follows, the invention and its advantages are further discussed on the basis of experimental measurements performed specifically on CO₂ electrolyzer cells constructed with one stack or three stacks, which are connected in the latter case in series/parallel.

As it was already discussed, the CO₂ electrolyzer cell according to the present invention is of a construction of at least one, preferably more than one stacks, i.e. its core which performs the electrolysis of CO₂ is built up of individual electrolyzer stacks connected electrically in series and in terms of the cell's gas management either in serial or in parallel configuration; the number of stacks used to construct the cell is up to even ten or

more, it ranges preferably from two to seven, more preferably from three to six, and most preferably it is three, or four, or five, or six.

Example 1 - Operation

In this example, some operational characteristics of a 3-stack cell assembled in serial configuration and then in parallel configuration (in terms of the cathode-side gas management) are compared with those of a 1-stack cell in brief.

Figure 13 illustrates the effects of the increase in the number of individual electrolyzer stacks used in a possible embodiment of the cell according to the invention assembled in either a serial or a parallel gas flow configuration. In particular, in plot (a), the CO₂ conversions during electrolysis at $\Delta U = -2.75$ V/stack achieved for a 1-stack and a 3-stack serial connected cell at different CO₂ feed rates are plotted. In plot (b), the CO₂ conversion during electrolysis at different cell voltages achieved for a cell consisting of one stack or three stacks, connected in parallel (with identical stack normalized gas feed), are shown. The series of measurements were performed feeding $T = 50^{\circ}\text{C}$ 1M KOH anolyte to the anode (at a feed rate of $1.5 \text{ dm}^3 \text{ min}^{-1}$). As for the cathode catalyst layer, 3 mg cm^{-2} Ag was immobilized on Sigracet39BC carbon paper by spray coating. As for the anode catalyst, 1 mg cm^{-2} Ir black was immobilized on a porous titanium frit. Both catalyst layers contained 15 wt% Sustanion ionomer. The cathode compartment was purged with humidified (in room temperature deionized water) CO₂. Furthermore, the CO₂ flow rate was set to $8.3 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$ for the measurements shown in (b).

As is clear from plot (a), when three electrolyzer stacks are coupled in series (compared to the 1-stack cell under the same conditions):

- the CO₂ conversion gets improved;
- this effect is more pronounced at higher flow rates; and
- a conversion of about 40% is achieved.

As is clear from plot (b), when three electrolyzer stacks are coupled in parallel (compared to the 1-stack cell under the same conditions):

- it is possible to increase the number of stacks without changing the operational features;
- inside the cell, the CO₂ stream is divided evenly; and

- the conversion and the CO partial currents are similar in the 3-stack configuration, which is a clear proof of the scalability of the process.

Figure 14 illustrates the current density versus the operational stack-voltage of a 3-stack CO₂ electrolyzer cell according to the invention used for syngas (H₂/CO mixture on Ag catalyst) or hydrocarbon (CH₄ and C₂H₄ on Cu catalyst) formation. The curves were recorded by linear sweep voltammetry (LSV) at $v = 10 \text{ mV s}^{-1}$ sweep rate with different catalyst containing cathode gas diffusion electrodes (GDEs). The series of measurements were performed feeding $T = 50^\circ\text{C}$ 1M KOH anolyte continuously to the anode compartment (at a feed rate of $\sim 9 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$), while the cathode compartment was purged with humidified (in room temperature deionized water) CO₂ at a flow rate of $u = 2.5 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$. As for the cathode catalyst layer, 1 mg cm^{-2} Ag was immobilized on Sigracet39BC carbon paper by spray coating. The Cu containing GDE was formed by electrodeposition. As for the anode catalyst layer, 1 mg cm^{-2} Ir black was immobilized on a porous titanium frit. Both catalyst layers contained 15 wt% Sustanion ionomer. Moreover, the cell was mounted with a spacer element of $300 \mu\text{m}$ in thickness.

Electrochemistry of the stacks proves the low voltage need. Due to the excellent electrical coupling among the various components of the cell, which is enhanced under pressure, the operational voltage of the cell is rather low (2.5 to 3.0 V). This translates to good energy efficiencies (40-50%). Syngas (H₂/CO mixture) formation was demonstrated on Ag/C catalyst, while ethylene production was demonstrated on a Cu/C catalyst.

Figure 15 demonstrates the stable operation of the electrolyzer cell. The shown chronoamperometric curve was taken at $\Delta U = -3 \text{ V/stack}$ for a 3-stack CO₂ electrolyzer cell according to the invention, using a 1 mg cm^{-2} Ag catalyst containing cathode GDE, immobilized on Sigracet39BC carbon paper by spray coating. As for the anode, 1 mg cm^{-2} Ir black was immobilized on a porous titanium frit. Both catalyst layers contained 15 wt% Sustanion ionomer. The cell was mounted with a spacer element of $270 \mu\text{m}$ in thickness. The measurement was performed feeding $T = 50^\circ\text{C}$ 1M KOH anolyte continuously to the anode compartment (at a feed rate of $\sim 9 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$), while the cathode compartment was purged with humidified (in room temperature deionized water) CO₂ at a flow rate of $u = 2.5 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$.

Figure 16 presents the formation of different gaseous CO₂-reduction products, generated using the electrolyzer cell with different catalysts. Gas chromatograms recorded during a chronoamperometric measurement at $\Delta U = -2.75$ V/stack performed with a 3-stack CO₂ electrolyzer cell according to the present invention are shown, using a spray coated, 3 mg cm⁻² Ag catalyst containing GDE [plot (a)] and Cu catalyst containing GDE, formed by electrodeposition of copper nanocubes on Sigracet39BC carbon paper [plot (b)]. As for the anode, 1 mg cm⁻² Ir black was immobilized on a porous titanium frit. The Ag containing GDE and the anode catalyst layer contained 15 wt% Sustanion ionomer. The cell was mounted with a spacer element of 270 μ m in thickness. The measurement was performed feeding T = 50°C 1M KOH anolyte continuously to the anode compartment (at a feed rate of ~ 9 cm³ cm⁻² min⁻¹), while the cathode compartment was purged with humidified (in room temperature deionized water) CO₂ at a flow rate of $u = 2.5$ cm³ cm⁻² min⁻¹.

Example 2 - Voltage dependent product distribution

The present example proves that the composition of the product syngas (H₂/CO ratio) can be simply tuned by the voltage of the cell. The higher the cell voltage, the more H₂ is generated.

Figure 17 shows partial current densities for CO and H₂ formation (ordinates to the left), as well as the ratio of the partial current densities (ordinates to the right) at different cell voltages (obtained by chronoamperometric and gas chromatography measurements), using a 3 mg cm⁻² Ag containing cathode GDE, immobilized on Sigracet39BC carbon paper by spray coating. As for the anode, 1 mg cm⁻² Ir black was immobilized on a porous titanium frit. Both catalyst layers contained 15 wt% Sustanion ionomer. The cell was mounted with a spacer element of 300 μ m in thickness. The measurements were performed feeding T = 50°C 1M KOH anolyte continuously to the anode compartment (at a feed rate of ~ 9 cm³ cm⁻² min⁻¹), while the cathode compartment was purged with humidified (in room temperature deionized water) CO₂ at a flow rate of $u = 2.5$ cm³ cm⁻² min⁻¹.

Example 3 – Effect of catalyst loading

The present example proves that the rate of carbon dioxide reduction strongly depends on the immobilized cathode catalyst amount. The partial current density for CO formation reaches a maximum at an intermediate catalyst loading.

Figure 18 shows partial current densities for H₂ and CO formation (ordinates to the left) and CO₂ conversion (ordinates to the right) during electrolysis at $\Delta U = -2.75$ V as a function of the Ag catalyst amount in the cathode GDE. The Ag cathode catalyst layer was immobilized on Sigracet39BC carbon paper by spray coating. As for the anode, 1 mg cm⁻² Ir black was immobilized on a porous titanium frit. Both catalyst layers contained 15 wt% Sustanion ionomer. The measurements were performed feeding T = 50°C 1M KOH anolyte continuously to the anode compartment (at a feed rate of ~ 9 cm³ cm⁻² min⁻¹), while the cathode compartment was purged with humidified (in room temperature deionized water) CO₂ at a flow rate of $u = 2.5$ cm³ cm⁻² min⁻¹.

10 Example 4 – Effect of cathode spacing (GDL compression)

The present example presents an additional benefit of the cell design according to the invention. By just changing one plastic element, the compression of the gas diffusion layer (GDL) can be varied. Notably, both the product distribution and the conversion are affected by this parameter. Importantly, if different GDLs have to be used, the cell can be quickly and easily tailored to it (unlike for the fuel-cell like setups, where the gas-sealing and compression of the GDL is achieved by using a gasket of a given thickness, which has to be carefully tailored to the GDE in hand).

Figure 19 shows partial current densities for H₂ and CO formation (ordinates to the left) and CO₂ conversion (ordinates to the right) during electrolysis at $\Delta U = -2.75$ V as a function of the applied cathode spacing. As for the cathode, 1 mg cm⁻² Ag cathode catalyst layer was immobilized on Sigracet39BC carbon paper by spray coating. As for the anode, 1 mg cm⁻² Ir black was immobilized on a porous titanium frit. Both catalyst layers contained 15 wt% Sustanion ionomer. The measurements were performed feeding T = 50°C 1M KOH anolyte continuously to the anode compartment (at a feed rate of ~ 9 cm³ cm⁻² min⁻¹), while the cathode compartment was purged with humidified (in room temperature deionized water) CO₂ at a flow rate of $u = 1.25$ cm³ cm⁻² min⁻¹.

Example 5 – Effect of flow pattern applied in the cathode current collector

The present example clearly shows that the flow pattern design (see Figure 9) has a prominent effect on the residence time of the CO₂ gas in the electrolyzer cell according to the invention, and hence on the cell performance. Here the effect of groove depth M (see

Figure 2B) is presented for the flow pattern of Figure 9(a). According to this example, there is an optimal groove-depth, and thus residence time, which ensures high conversion rates.

Figure 20 shows partial current densities for H₂ and CO formation (ordinates to the left) and CO₂ conversion (ordinates to the right) during electrolysis at $\Delta U = -2.75$ V as a function of the depth M of the grooves of the flow-pattern applied in the cathodic side of the electrolyzer cell according to the invention. As for the cathode, 3 mg cm⁻² Ag cathode catalyst layer was immobilized on Sigracet39BC carbon paper by spray coating. As for the anode, 1 mg cm⁻² Ir black was immobilized on a porous titanium frit. Both catalyst layers contained 15 wt% Sustanion ionomer. The measurements were performed feeding T = 50°C 1M KOH anolyte continuously to the anode compartment (at a feed rate of ~ 9 cm³ cm⁻² min⁻¹), while the cathode compartment was purged with humidified (in room temperature deionized water) CO₂ at a flow rate of $u = 2.5$ cm³ cm⁻² min⁻¹.

Example 6 – Effect of carbon dioxide flow rate in the electrolyzer cell

The present example is to prove that an increasing CO₂ flow rate increases the conversion rate (current density) of the electrolyzer cell according to the invention. At the same time, the relative ratio of the converted CO₂ to the feed-rate decreases (thus an optimal value for the CO₂ flow rate has to be found and used).

Figure 21 illustrates partial current densities for H₂ and CO formation (ordinates to the left) and CO₂ conversion (ordinates to the right) during electrolysis at $\Delta U = -2.75$ V as a function of carbon-dioxide flow rate (normalized with the surface area) in the cathode compartment of the electrolyzer cell according to the invention. Again, as for the cathode, 3 mg cm⁻² Ag cathode catalyst layer was immobilized on Sigracet39BC carbon paper by spray coating. As for the anode, 1 mg cm⁻² Ir black was immobilized on a porous titanium frit. Both catalyst layers contained 15 wt% Sustanion ionomer. The measurements were performed feeding T = 50°C 1M KOH anolyte continuously to the anode compartment (at a feed rate of ~ 9 cm³ cm⁻² min⁻¹).

Example 7 – Effect of anolyte (cell) temperature

The present example is to prove that high reaction rate and selectivity can be achieved at elevated temperatures, which can easily be regulated by the anolyte

temperature. Importantly, the components of the electrolyzer cell are designed to withstand exposure to hot (alkaline) solutions, as exemplified in this case.

Figure 22 shows partial current densities for H_2 and CO formation (ordinates to the left) and CO_2 conversion (ordinates to the right) during electrolysis at $\Delta U = -2.75$ V as a function of the anolyte (1M KOH) temperature (at a feed rate of $\sim 9 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$) taking place in the electrolyzer cell according to the invention. The cathode compartment was purged with humidified (in room temperature deionized water) CO_2 at a flow rate of $u = 2.5 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$. Again, as for the cathode, 3 mg cm^{-2} Ag cathode catalyst layer was immobilized on Sigracet39BC carbon paper by spray coating. As for the anode, 1 mg cm^{-2} Ir black was immobilized on a porous titanium frit. Both catalyst layers contained 15 wt% Sustanion ionomer.

Example 8 – Effect of pressure in the electrolyzer cell

The present example is to prove that at lower cell voltages the CO_2 reduction, while at larger cell voltages the water reduction is the dominant cathode process. The cross-over between the two processes is shifted to larger current densities by increasing the CO_2 pressure, allowing CO_2 electroreduction to proceed at higher rates. The slope of the LSV curve at lower cell voltages increases gradually with the CO_2 pressure. Hence, lower cell voltages are required to achieve the same current density under pressurized operation of the electrolyzer cell. This is further highlighted by tracing the LSV curves – recorded at different CO_2 pressures – at given cell voltages.

Figure 23 presents LSV curves recorded at $v = 10 \text{ mV s}^{-1}$ sweep rate under various differential CO_2 pressures ranging from 1 bar to 10 bar during electrolysis performed in the electrolyzer cell according to the invention. Again, as for the cathode, 3 mg cm^{-2} Ag cathode catalyst layer was immobilized on Sigracet39BC carbon paper by spray coating. As for the anode, 1 mg cm^{-2} Ir black was immobilized on a porous titanium frit. The measurements were performed feeding $T = 50^\circ\text{C}$ 1M KOH anolyte continuously to the anode compartment (at a feed rate of $\sim 9 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$), while the cathode compartment was purged with humidified (in room temperature deionized water) CO_2 at a flow rate of $u = 12.5 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$.

Furthermore, Figure 24 shows current densities at different cell voltages (plot A) and the ratio of the partial current densities (plot B) during electrolysis at $\Delta U = -2.75$ V, both as a function of the differential CO_2 pressure prevailing in the electrolyzer cell when it continuously operates. Again, as for the cathode, 3 mg cm^{-2} Ag cathode catalyst layer was immobilized on Sigracet39BC carbon paper by spray coating. As for the anode, 1 mg cm^{-2} Ir black was immobilized on a porous titanium frit. The measurements were performed feeding $T = 50^\circ\text{C}$ 1M KOH anolyte continuously to the anode compartment (at a feed rate of $\sim 9 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$), while the cathode compartment was purged with humidified (in room temperature deionized water) CO_2 at a flow rate of $u = 12.5 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$.

Figure 24 suggests that the selectivity for CO production is significantly increased by the increased CO_2 pressure. Hence, this further allows controlling the syngas product composition (H_2/CO ratio).

Brief summary

As is clear from the afore-mentioned, the present invention provides/exhibits:

- Electrochemical cell architecture for the efficient electrochemical conversion of carbon dioxide.
- Pressure handling up to 30 bar (preferably 20 bar), through the cathode-side and anode-side pressure chambers.
- Pressure tolerance, i.e. pressure applied to the electrolyzer cell improves the coordination of various cell components, sealing elements and electrical contacts by compensating the negative effects of imperfect matches in the dimensions of the components due to fabrication, and thus, results in enhanced cell performance.
- High mechanical strength components (e.g. stainless steel, titanium, metal alloys or composite material framework).
- Specific sealing system, including O-rings seated in recesses/grooves and a pressure chamber both at the anodic and the cathodic sides.
- Highly scalable cell construction, both in terms of size or physical dimensions, number of the stacks and product yields due to modular construction.
- Multi-stack construction in serial and parallel gas feed (important for scaling up), meaning that the initial CO_2 gas stream is either (i) divided within the cell and fed

to all stacks (parallel conversion takes place at various stacks), or (ii) the whole CO₂ feed go through all the stacks, one after the other (serial design).

- The above two scenarios (i.e. serial or parallel gas management at the cathodic side) is realized with the same cell construction elements, just by different assembling which is ensured by the modular construction of the electrolyzer cell and the multifunctionality of the elements, in particular, of the anode-side spacer element, the very specific design of which allows the serial or parallel gas management in the same cell.
- The modularity of the cell allows to combine these two scenarios, hence to connect some of the electrolyzer stacks in parallel, while others in series in the same cell.
- Modularity also ensures the use of different ion exchange membranes, gas diffusion layers and catalysts, without changing the overall architecture (but still maintaining pressure tolerance).
- High conversion rates as a consequence of
 - direct gas feed,
 - high pressure capability,
 - controlled residence time (with cell geometry),
 - specific flow patterns (central feed of CO₂, radial collection of products).
- Novel design for connecting multiple individual stacks to each other in order to facilitate gas and liquid transport within the electrolyzer cell.
- Wide variety of catalysts are usable in the electrolyzer, including but not limited to Sn, Pb, Ag, Cu, Au, C, Fe, Co, Ni, Zn, Ti, Mn, Mo, Cr, Nb, Pt, Ir, Rh, Ru, and different binary compositions and oxides formed thereof.
- Multitude of different products formed in different compositions, including but not limited to hydrogen, carbon monoxide, ethylene, methane.
- Capability of producing, also on the industrial scale, e.g. syngas and ethylene in CO₂ electrolyzer cells with Ag/C catalyst and Cu/C catalyst, respectively.
- Possibility for the optimization of the operational parameters (input flow rate, humidification, pressure, cell temperature, flow pattern and its depth, GDL compression).
- Tunable syngas composition is achievable simply by changing the cell voltage.

Furthermore, as is also clear to a person skilled in the art, the present inventive solutions, either considered alone or in any combination, are not limited to the exemplified embodiments, i.e. the electrolyzer cells for converting gaseous carbon dioxide, but can also be applied in other electrochemical setups (such as e.g. N₂-reduction to ammonia).

- 5 In light of the afore-mentioned, from a technological perspective, assembling multi-stack electrolyzers similar to the one illustrated in Figure 1 instead plurality of single-stack cells operating in parallel decreases the capital investment costs, as the cell frame and the anolyte circulation loop has to be built only once, and the inclusion of a further stack only requires an additional bipolar plate assembly, some sealing elements and
- 10 an additional membrane electrode assembly.

CLAIMS

1. An electrolyzer cell (100', 100'') to convert gaseous carbon dioxide, CO₂, to at least one gas-phase product that leaves the electrolyzer cell (100', 100''), comprising
- a cathode-side end unit (26) with a gas inlet (21), a fluid inlet (23), a fluid outlet (24) and an electrical terminal;
 - an anode-side end unit (27) with a gas outlet (22) and an electrical terminal;
 - at least two electrolyzer stacks (40) sandwiched between the cathode-side end unit (26) and the anode-side end unit (27), each electrolyzer stack (40) comprising
 - a cathode current collector (5; 5a, 5b, 5c, 5d);
 - an anode current collector (10);
 - a membrane electrode assembly comprising
 - an ion-exchange membrane (7) with a first side and a second side,
 - a layer of cathode catalyst (6b) arranged on said first side in contact with the membrane (7),
 - a cathode-side gas diffusion layer (6a) arranged on the layer of cathode catalyst (6b) in contact with the cathode catalyst (6b),
 - a layer of anode catalyst (8b) arranged on said second side in contact with the membrane (7),
 - an anode-side gas diffusion layer (8a) arranged on the layer of anode catalyst (8b) in contact with the anode catalyst (8b);
 - a spacer element (9a, 9b), said spacer element (9a, 9b) is configured to fix the membrane electrode assembly between the cathode current collector (5; 5a, 5b, 5c, 5d) and the anode current collector (10) sandwiched between the cathode current collector (5; 5a, 5b, 5c, 5d) and the anode current collector (10), wherein
 - the cathode-side gas diffusion layer (6a) is in partial contact with the cathode current collector (5; 5a, 5b, 5c, 5d) thereby forming a cathode-side in-plane flow structure (5'') therebetween, and
 - the anode-side gas diffusion layer (8a) is in partial contact with the anode current collector (10) thereby forming an anode-side in-plane flow structure (5') therebetween;

to separate the cathode current collector (5; 5a, 5b, 5c, 5d) and the anode current collector (10) from one another;

a sealed continuous stack gas flow path extending between a stack gas inlet (46) and a stack gas outlet (47) within the stack (40) through the cathode-side flow structure (5'');
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a sealed continuous stack fluid flow path extending between a stack fluid inlet (48) and a stack fluid outlet (49) within the stack (40) through the anode-side flow structure (5'); wherein

- the electrical terminal of the cathode-side end unit (26), the at least two electrolyzer stacks (40) and the electrical terminal of the anode-side end unit (27) are connected electrically in series; and
10
- the stack gas flow paths of the electrolyzer stacks (40) with gas transport channels (34, 35) extending between adjacent stacks (40) through the cathode current collector (5; 5a, 5b, 5c, 5d), the spacer element (9a, 9b) and the anode current collector (10) form a continuous gas flow path that extends from the gas inlet (21) to the gas outlet (22) to supply CO₂ to each cathode-side gas diffusion layer (6a) to convert the CO₂ to the gas-phase product via at least one cathodic electrolysis reaction taking place in the cathode-side flow structure (5'') of each electrolyzer stack (40), and to discharge the product through said gas outlet (22), and
15
- the stack fluid flow paths of the electrolyzer stacks (40) with fluid transport channels (38, 39) extending between adjacent stacks (40) through the cathode current collector (5; 5a, 5b, 5c, 5d), the spacer element (9a, 9b) and the anode current collector (10) form a continuous fluid flow path that extends from the fluid inlet (23) to the fluid outlet (24) to supply liquid anolyte to each anode-side flow structure (5') to complete said cathodic electrolysis reaction with at least one anodic electrolysis reaction taking place at the anode-side flow structure (5') of each electrolyzer stack (40), and to discharge the liquid-phase anolyte and reaction product(s) forming in said anodic electrolysis reaction through said fluid outlet (24).
20
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2. The electrolyzer cell (100', 100'') according to claim 1, wherein

at least two stack gas flow paths of the electrolyzer stacks (40) are connected to one another in series and the remaining stack gas flow paths of the electrolyzer stacks (40) are connected to one another in parallel; or

at least two stack gas flow paths of the electrolyzer stacks (40) are connected to one another in parallel and the remaining stack gas flow paths of the electrolyzer stacks (40) are connected to one another in series.

3. The electrolyzer cell (100', 100'') according to claim 2, wherein the spacer element (9a, 9b) comprises an internal gas transport channel (36) passing therethrough in a first peripheral region of the spacer element (9a, 9b), said spacer element (9a, 9b) further comprising a second peripheral region located diametrically opposite to the first peripheral region, said second peripheral region being configured to act as means for selectively choose the way two adjacent stack flow paths connect to one another in the gas flow path of the electrolyzer cell (100', 100'').

4. The electrolyzer cell (100', 100'') according to claim 3, wherein said second region comprises a further internal gas transport channel (36) as said means.

5. The electrolyzer cell according to any of claims 1 to 4, wherein
a cathode-side pressure chamber (31) is formed in the cathode-side end unit (26),
and
an anode-side pressure chamber (32) is formed in the anode-side end unit (27),
wherein
said gas flow path is directed through the cathode-side pressure chamber (31) and the anode-side pressure chamber (32) to provide adaptive pressure control on the electrolyzer stacks (40) and thus to provide uniform pressure distribution throughout said electrolyzer stacks (40).

6. The electrolyzer cell according to any of claims 1 to 5, wherein
the cathode current collector (5; 5a, 5b, 5c, 5d) of each electrolyzer stack (40) is formed as a second component (40b) of a two-component bipolar plate assembly (40'), and
the anode current collector (10) of each electrolyzer stack (40) is formed as a first component (40a) of the two-component bipolar plate assembly (40').

7. The electrolyzer cell according to any of claims 1 to 6, wherein the cathode current collector (5; 5a,5b,5c,5d) of each electrolyzer stack (40) comprises a system of flow-channels (5'') in a surface thereof facing the membrane (7) arranged to provide even gas distribution over the cathode-side gas diffusion layer (6a).

5 8. The electrolyzer cell according to any of claims 1 to 7, wherein the anode current collector (10) of each electrolyzer stack (40) comprises a system of flow-channels (5') in a surface thereof facing the membrane (7) arranged to provide even fluid distribution over the anode-side gas diffusion layer (8a).

9. The electrolyzer cell according to any of claims 1 to 8, wherein the anode-side
10 gas diffusion layer (8a) of each electrolyzer stack (40) is chosen from a group consisting of Ti-frits in the form of pressed Ti powder of different average particle size, Ni-frits in the form of pressed Ni powder of different average particle size, Ti-mesh and Ni-mesh.

10. The electrolyzer cell according to any of claims 1 to 9, wherein the cathode catalyst (6b) is chosen from a group consisting of Ag/C catalyst and Cu/C catalysts.

15 11. The electrolyzer cell according to any of claims 1 to 10, wherein the anode catalyst (8b) is chosen from a group consisting of IrO_x, RuO_x, NiO_x and TiO_x.

12. The electrolyzer cell (100', 100'') according to any of claims 1 to 11, wherein the number of the electrolyzer stacks (40) is at most ten, ranges preferably from three to seven, more preferably from three to six.

20 13. An electrolyzer setup (200) to convert gaseous carbon dioxide, CO₂, to at least one gas-phase product, the setup (200) comprising
 an electrolyzer cell (100', 100'') according to any of claims 1 to 12;
 a source (201) of gaseous CO₂;
 a source of liquid anolyte (213);
25 an external power source (220) with a first pole of a first electrical charge and a second pole of a second electrical charge, the second electrical charge being opposite in sign compared to the first electrical charge; the first pole electrically coupled to the electrical terminal of the cathode-side end unit (26) of the electrolyzer cell (100', 100'')

and the second pole electrically coupled to the electrical terminal of the anode-side end unit (27) of the electrolyzer cell (100', 100'');

a cathode-side circulation assembly to circulate the gaseous CO₂ from said source (201) of gaseous CO₂ through the gas flow path of the electrolyzer cell (100', 100'') to at least one product receptacle; and

an anode-side circulation assembly to circulate the liquid anolyte (213) from said source of liquid anolyte (213) and through the fluid flow path of the electrolyzer cell (100', 100'').

14. The electrolyzer setup (200) according to claim 13, wherein the cathode-side circulation assembly further comprises a humidifier (203) arranged upstream of the electrolyzer cell to humidify the CO₂ before being supplied into the electrolyzer cell (100', 100'').

15. The electrolyzer setup (200) according to claim 13 or 14, wherein the cathode-side circulation assembly further comprises a back-pressure regulator (209) arranged downstream of the electrolyzer cell (100', 100'') to increase the pressure difference prevailing in the electrolyzer cell (100', 100'').

16. The electrolyzer setup (200) according to any of claims 13 to 15, wherein the cathode-side circulation assembly further comprises a water separator (208) arranged downstream of the electrolyzer cell (100', 100'') and upstream of the back-pressure regulator (209) to remove moisture from the gaseous product(s).

17. The electrolyzer setup (200) according to any of claims 13 to 16, wherein the anode-side circulation assembly also comprises a liquid anolyte refreshing unit (211) to refresh the anolyte (213), if needed, and/or to separate the reaction product(s) forming in the anodic electrolysis reaction(s) from the anolyte (213).

18. The electrolyzer setup (200) according to claim 17, wherein the anolyte refresher unit (211) is in thermal coupling with a tempering means (212) to adjust the temperature of the anolyte (213).

19. The electrolyzer setup (200) according to any of claims 13 to 18, wherein the anolyte is an aqueous KOH solution.

20. The electrolyzer setup (200) according to any of claims 13 to 19, wherein the cathode catalyst is Ag/C and the gas-phase product is a mixture of hydrogen and carbon monoxide.

21. The electrolyzer setup (200) according to any of claims 13 to 20, wherein the
5 cathode catalyst is Cu/C and the gas-phase product is ethylene.

22. A method to convert gaseous carbon dioxide, CO₂, to at least one gas-phase product, comprising the steps of

providing an electrolyzer cell (100', 100'') according to any of claims 1 to 12;

by employing said electrolyzer cell, assembling an electrolyzer setup (200)
10 according to any of claims 13 to 21;

circulating gaseous CO₂ through the electrolyzer cell (100', 100'') of the electrolyzer setup (200);

simultaneously with circulating CO₂, circulating liquid anolyte (213) through the electrolyzer cell (100', 100'') of the electrolyzer setup (200); and

15 while keeping the CO₂ and the anolyte in circulation, performing cathodic electrolysis reactions and anodic electrolysis reactions in the electrolyzer cell (100', 100'') to convert the gaseous CO₂, in continuous flow, to the at least one gas-phase product;

separating the at least one gas-phase product from the gaseous CO₂;

optionally, if needed, refreshing the anolyte (213); and

20 discharging the at least one gas-phase product from the electrolyzer setup (200).