(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 4 512 934 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
26.02.2025 Bulletin 2025/09

(21) Application number: **23192695.7**

(22) Date of filing: **22.08.2023**

(51) International Patent Classification (IPC):
C25B 3/03 *(2021.01)* ***C25B 3/26*** *(2021.01)*
C25B 9/21 *(2021.01)* ***C25B 9/23*** *(2021.01)*
C25B 11/032 *(2021.01)* ***C25B 11/043*** *(2021.01)*
C25B 11/077 *(2021.01)* ***C25B 13/02*** *(2006.01)*
C25B 13/05 *(2021.01)* ***C25B 13/08*** *(2006.01)*

(52) Cooperative Patent Classification (CPC):
C25B 3/26; C25B 3/03; C25B 9/21; C25B 9/23;
C25B 11/032; C25B 11/043; C25B 11/077;
C25B 13/02; C25B 13/05; C25B 13/08

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL
NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

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(54) NOVEL MEMBRANE ELECTRODE ASSEMBLY DESIGN FOR C2H4 SELECTIVE CEM-TYPE CO2-ELECTROLYZERS

(57) The present invention pertains to a membrane assembly, in particular a membrane electrode assembly, for CO_2 electrolysis in a zero-gap cell, as well as a corresponding zero-gap cell and method for producing such membrane assembly. Accordingly, a membrane assembly (10) for supporting CO_2 electrolysis in a zero-gap cell electrolyzer is suggested, comprising an anion exchange ionomer layer, wherein said anion exchange ionomer layer comprises microparticles and/or nanoparticles at a weight percent between 1 wt. % and 50 wt. %, wherein the microparticles and/or nanoparticles comprise or are formed of a metal oxide.

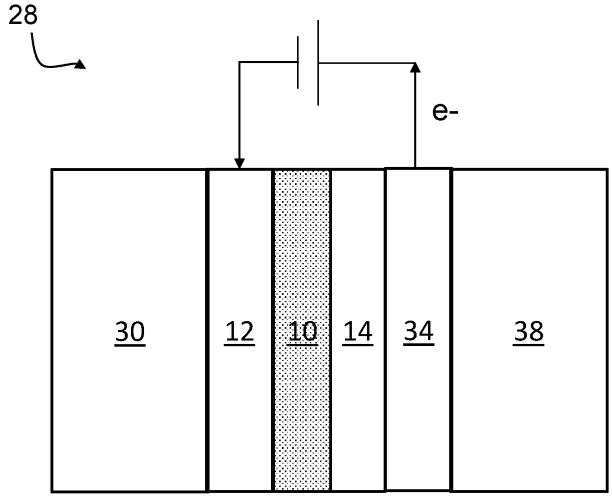

Fig. 2

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Description

Technical Field

[0001] The invention relates to a membrane assembly, in particular a membrane electrode assembly, for carbon dioxide (CO_2) electrolysis in a zero-gap cell, as well as a corresponding zero-gap cell and method for producing such membrane assembly.

Technological Background

[0002] Electrochemical CO_2 reduction reaction (CO_2RR) to hydrocarbons poses a promising alternative to other energy storage strategies in the future. The conversion of CO_2 by electrochemistry is an attractive means by which renewable electricity, such as solar energy and wind energy, can be used and CO_2 can be bound as a product. However, it has been a challenge to develop systems that are sufficiently selective, efficient and stable, in particular in view of selective hydrocarbon formation.

[0003] In this regard, catalysts for CO_2 reduction reaction can particularly suffer from poor stability of the desired products' formation. From the group of potential catalysts including e.g. copper (Cu), silver (Ag), gold (Au), palladium (Pd), tin (Sn), copper is the only transition metal catalyst for CO_2RR to value added C_2+ products, such as ethylene, ethanol, or propanol. Such copper-based catalysts are commonly used on the cathode side of the electrochemical cells.

[0004] In the cathode, CO_2 may be reduced to a variety of compounds, including carbon monoxide, formate, ethylene, ethanol, propanol and some other minor products, such as methane or allyl alcohol. However, undesired side reactions typically occur at the cathode, including a hydrogen evolving reaction (HER). In this regard, the thermodynamical equilibrium potentials versus standard hydrogen of the above-mentioned reactions unfortunately suggest that the CO_2 reduction to CO_2RR products and the occurrence of hydrogen formation are thermodynamically favored in the same and very narrow potential range.

[0005] While copper-based cathode electrodes may theoretically be implemented in various electrolyzer cell architectures, not all of these architecture designs are compatible for use with a CO_2 electrolyzer. For example, an electrolyzer cell architecture that has been implemented both in research and on larger scale in industrial electrolyzer cells is a cation exchange membrane (CEM) based zero-gap cell. While such design hence readily enables scalability, zero-gap cells are contemplated for water electrolysis. In accordance, it has been found that the cation exchange membrane interfacial microenvironment entirely inhibits the CO_2 reduction reaction while promoting the hydrogen evolving reaction, such that attempts to implement copper-based cathode electrodes in such cells have so far been unsuccessful.

[0006] In particular, it was found on the level of the cation exchange membrane that the membrane develops an acidic surface due to the dissolved sulfonate side chains of the per-fluorosulfonic acid (PFSA) backbone. These side chains form spherically shaped ionic clusters, which associate protons, thereby accumulating several hydronium ions per sulfonate group. As a result, a pH shift occurs towards acidic values in the membrane vicinity, wherein these local acidic conditions in the cathode electrode proximity increase the kinetic overpotentials for CO_2 reduction reactions, leading to an almost exclusive selectivity to the competing and undesired hydrogen evolving reaction.

[0007] So far efforts have been made to resolve these challenges, for example, by implementing an anion exchange membrane. However, for anion exchange membranes there exists an intrinsic efficiency problem, since the CO_2 feed is turned into carbonate and bicarbonate in alkaline conditions and the anions are hence transferred through the anion exchange membrane, leading to CO_2 losses and undesired salt formation. On the other hand, carbon exchange membranes can ensure an almost CO_2 free anode, thereby minimizing CO_2 losses. Other efforts aiming at strong acidic conditions with the presence of potassium ions have not been found to provide prolonged stability.

[0008] Accordingly, a need exists to improve the reaction conditions and microenvironment necessary for CO_2 reduction reactions and, in particular, to abrogate the issues in widely used CEM-based zero-gap cells inhibiting CO_2 reduction reactions to facilitate industrial scalability for CO_2 electrolysis.

Summary of the invention

[0009] It is an object of the present invention to provide an improved mechanism enabling CO_2 reduction, in particular in zero-gap cells.

[0010] Accordingly, in a first aspect, a membrane assembly for supporting CO_2 electrolysis in a zero-gap cell electrolyzer is suggested, comprising an anion exchange ionomer layer, wherein said anion exchange ionomer layer comprises microparticles and/or nanoparticles at a weight percent between 1 wt. % and 50 wt. %, wherein the microparticles and/or nanoparticles comprise or are formed of a metal oxide.

[0011] By means of the membrane assembly, an additional layer may be provided in zero-gap electrochemical cells that are commonly used for water electrolysis. The anion exchange ionomer layer or membrane layer is particularly suitable for implementation between a cathode catalyst layer and a cation exchange membrane of the zero-gap cell. Due to the presence of the anion exchange ionomer, anions may be efficiently transported and hence local (moderate) alkaline conditions may be employed. In particular, the anion exchange ionomer layer accommodates the OH- being produced in the cathode and creates a more alkaline local environment for the cathode due to the corresponding higher local pH, which was found to be beneficial for the desired C-C coupling reaction mechanism yielding ethylene (C_2H_4), for example, as a product.

[0012] At the same time, this provides an effective shielding of said cathode catalyst against hydrogen ions or protons being produced in the anode. Accordingly, harsh acidic environments of the cation exchange membrane may be effectively avoided at the level of the copper-based cathode catalyst.

[0013] In addition, the mixture of the anion exchange ionomer layer with nanoparticles and/or microparticles results in a predefined porosity of the anion exchange ionomer layer. This permits the CO_2 gaseous molecules, which are formed by the carbonate anions at the cation exchange membrane interface, to diffuse back to the catalyst layer and/or gas feed chamber. Accordingly, this facilitates the provision of effective three-phase boundaries by mediating the CO_2 to the cathode catalyst layer.

[0014] In this regard, together with the predefined porosity, the amount of anion exchange ionomer used in this layer also optimizes the hydrophobicity of the respective layer as well as their water uptake capacity due to their swelling nature. This is because the anion exchange ionomer materials are preferably formed of a hydrophobic polymer backbone with a hydrophilic ion exchange functional group. Accordingly, the provision of sufficient three-phase boundaries may be further ensured by means of the corresponding hydrophobicity and e.g. a reduced water availability potentially blocking said three-phase boundaries.

[0015] Preferably, the anion exchange ionomer may be provided by a polymer named 1H-Imidazole, 1,2,4,5-tetramethyl-, compd. with 1-(chloromethyl)-4-ethenylbenzene polymer with ethenylbenzene. Said polymer has been found to achieve the above technical advantages while simultaneously being suitable for processing and production of the anion exchange ionomer layer. However, similar polymers as anion exchange ionomers enabling the transport of anions and which employ local alkaline conditions may be implemented.

[0016] The membrane assembly according to the invention hence effectively solves the problem of an unfavorable cation exchange membrane-catalyst microenvironment which inhibits CO_2 reduction reactions while furthermore improving the selectivity of said reduction reactions to C-C coupling, yielding an increased proportion of value-added ethylene (C_2H_4), for example, as a product. Furthermore, the elaborate use of the anion exchange ionomer and microparticles and/or nanoparticles in specific amounts impairs the CO_2 crossover to anode avoids delamination, which have been found to constitute main disadvantages of alternative methods including the implementation of anion exchange membranes, for example. Thereby, the membrane assembly may be implemented in a CEM-based zero-gap cell architecture, which already exist in industrial products, thereby establishing a high technology readiness level with the potential of accelerating the commercialization of CO_2 electrolyzers.

[0017] Preferably, the microparticles and/or nanoparticles are present in the anion exchange ionomer layer at a weight percent between 5 wt. % and 35 wt. %, preferably between 15 wt. % and 25 wt. %. Said ranges have been found to be particularly advantageous to provide a predefined level of porosity facilitating the transfer of CO_2 to the cathode catalyst layer, when implemented in a cell. Thereby, the production of hydrocarbons from CO_2 is further favored without significantly affecting the alkaline barrier established by the anion exchange ionomers.

[0018] The anion exchange ionomer layer or membrane layer may be formed as a single layer or may be formed as multiple sublayers forming a continuous stack by material bonding. For example, layers may be successively applied on top of each other to achieve a predefined thickness or height of the membrane layer in a controlled and/or variable manner. Alternatively, or in addition, different layers may be formed on top of each other, wherein one or more layers comprise a different weight percent of the microparticles and/or nanoparticles. Thereby, the porosity may be varied and/or a gradient of the microparticles and/or nanoparticles and anion exchange ionomers may be provided as desired for the respective application in a zero-gap cell.

[0019] The microparticles and/or nanoparticles preferably have a size between 10 nm and 80 pm, wherein said particles preferably have an essentially uniform size. The term "essentially uniform" is to be understood to include manufacturing tolerances and size distributions and may e.g. include relative tolerance ranges up to 20 percent, preferably up to 5 percent, such that e.g. more than 90 percent of the particles are e.g. within the range of 10 nm to 120 nm or between 1 μm and 10 μm.

[0020] The particular particle size or particle size distribution may be chosen e.g. depending on the production method and/or the predefined porosity to be achieved for the anion exchange ionomer layer of the membrane assembly.

[0021] In particular, the nanoparticles or microparticles may respectively have a size between 10 nm and 120 nm or between 1 μm and 10 μm, e.g. between 3 μm and 7 μm.

[0022] Such combination of the particular particle size and in combination with the preferred weight percent has been found to be particularly advantageous to achieve CO_2 reduction reactions with a significant increase e.g. in value-added ethylene production.

[0023] The microparticles and/or nanoparticles may comprise and are preferably formed of a transition metal or metalloid, such as titanium dioxide, zirconium dioxide, cerium dioxide, aluminium oxide, yttrium oxide, or silicon dioxide. The use of metal oxide for the particles, e.g. titanium dioxide, may be advantageous to catalyze the possible reaction of water splitting occurring at the cation exchange membrane and anion exchange ionomer layer conjunction. Thereby, overpotentials occurring at said conjunction may be avoided and lower cell potentials may be achieved, which favor the production of hydrocarbons from CO_2. Alternatively, the microparticles and/or nanoparticles may be formed of carbon nanoparticles, graphite, or graphene or inert particles, such as small fiberglass particles, PFA particles, PTFE particles, or PEEK particles.

[0024] The anion exchange layer may be formed by a variety of manufacturing techniques. Preferably, the anion exchange layer is formed by physical vapor deposition, chemical vapor deposition, drop casting, spray coating, or dry and hot pressing. By means of the production method, the porosity and distribution of the microparticles and/or nanoparticles and anion exchange ionomers may be predefined and controlled. For example, the anion exchange ionomer and microparticles and/or nanoparticles may be provided as an ink for drop casting, spray coating, physical vapor deposition, or chemical vapor deposition, e.g. using a solvent, or may be provided as a paste suitable for dry pressing, wherein the ink and paste as well as the corresponding application method may define the level of porosity. Accordingly, a fine tuning of the characteristics of the membrane assembly may be provided with regard to the permeation of CO_2 and the availability of three-phase boundaries at the cathode catalyst layer.

[0025] In order to facilitate the implementation in CEM-based zero-gap cells, the membrane assembly preferably comprises a catalyst layer comprising a copper-based cathode catalyst, which together form a cathode electrode portion for a membrane electrode assembly. Thereby, the cathode electrode portion may be simply combined with an anode half of a zero-gap cell or half a membrane electrode assembly, i.e. the cation exchange membrane and the adjacent anode catalyst layer, so as to form a membrane electrode assembly.

[0026] The membrane assembly including the catalyst layer may be may be considered as a stack of layers and may optionally include a gas diffusion layer adjacent to the cathode catalyst layer at a side opposing the anion exchange ionomer layer. Accordingly, gaseous CO_2, which is preferably wet or humidified, may pass through the optionally included gas diffusion layer first before reaching the catalyst layer and the adjacent anion exchange ionomer layer. The catalyst layer is copper-based and is preferably formed of copper-oxide (CuO) or paramelaconite Cu_4O_3.

[0027] Preferably, the anion exchange layer has been directly formed on the catalyst layer. For example, the anion exchange layer comprising microparticles and/or nanoparticles may have been formed on the catalyst layer by drop casting or other techniques to provide a direct material and/or mechanical bonding. In this manner, a more mechanically and electrically stable membrane assembly may be provided, optionally including a gas diffusion layer with a predefined pore size adapted for CO_2 diffusion, so as to form a gas diffusion electrode. The direct application furthermore may result in an even more effective shielding of the cathode catalyst layer against hydrogen ions or protons being produced in the anode.

[0028] The catalyst layer may comprise a predefined amount of anion exchange ionomer. The use of anion exchange ionomers in the active catalyst layer, which preferably forms an inner layer of the membrane electrode assembly, was found to limit the availability of potassium ions (K+) inside this layer. As a result, in particular in the active catalyst layer and in the gas diffusion layer, the coexistence of potassium ions and carbonate anions is effectively avoided.

[0029] Thereby, the occurrence or likelihood of typical salt formation resulting from the coexistence of potassium ions and carbonate anions in the active catalyst layer and in the gas diffusion layer is significantly reduced, improving the durability, stability and efficiency of the cathode catalyst layer. To avoid that the application of the anion exchange ionomers potentially results in a blocking of the pores of the gas diffusion layer, the anion exchange ionomer is preferably arranged at a side of the catalyst layer opposing the gas diffusion layer, i.e. adjacent to the anion exchange ionomer layer.

[0030] The membrane assembly may optionally comprise a conductive layer arranged between the catalyst layer and the anion exchange layer, wherein the catalyst layer and the conductive layer together form a gas diffusion electrode, and wherein the conductive layer comprises at least one layer comprising a predefined amount of cation exchange ionomer so as to form a bipolar gas diffusion electrode.

[0031] The conductive layer may be arranged in a stacked formation at a side of the catalyst layer so as to be adjacent to the anion exchange ionomer layer, i.e. opposing the side of the catalyst layer being adjacent to the optional gas diffusion layer.

[0032] By means of the anion exchange ionomers and the cation exchange ionomers at the level of the cathode, a bipolar electrode may be implemented in the membrane assembly. This has been found to be particularly advantageous to enable the desired selectivity and stability of the CO_2 reduction reactions. In particular, the use of cation exchange ionomers in the conductive layer of the electrode, which preferably is formed as an outer layer, may provide a further enrichment of OH-anions in the active catalyst layer, so as to further improve the alkaline environment due to the corresponding higher local pH, as described above in view of the anion exchange ionomer layer. Furthermore, the use of these cation exchange ionomers in the conductive layer impairs the carbonate anion availability in the adjacent catalyst layer, thereby further reducing the coexistence of potassium ions and carbonate anions and reducing the occurrence or likelihood of the corresponding salt formation.

[0033] In addition, while the implementation of both anionic and cationic exchange ionomers ensures that the required level of permeance of anions or cations may be provided, it also optimizes the hydrophobicity of the respective layer as well as their water uptake capacity due to their swelling nature. This is because, as described above in view of the anion exchange ionomer layer, the ion exchange materials are preferably formed of a hydrophobic polymer backbone with a hydrophilic ion exchange functional group. Accordingly, the provision of sufficient three-phase boundaries may be further ensured and/or defined by means of the corresponding hydrophobicity and e.g. a reduced water availability within pores of the gas diffusion layer.

[0034] The weight percent of anion exchange ionomer in de catalyst layer is preferably between 0.1 wt. % and 25 wt. %, preferably between 5 wt. % and 15 wt. %, wherein the amount of cation exchange ionomer in the conductive layer preferably corresponds to the amount of anion exchange ionomer. In particular, the conductive layer may comprise a carbon nanoparticle layer, wherein the weight percent of cation exchange ionomer for said layer is between 0.1 wt. % and 25 wt. %, preferably between 2.5 wt. % and 7.5 wt. %.

[0035] The hydrophobicity and polarity of the cathode electrode is preferably balanced between the different layers. Accordingly, the weight percent of anion exchange ionomer in the cathode catalyst layer and the weight percent of cation exchange ionomer in the conductive layer are preferably essentially the same and/or the amount of anion exchange ionomer in the cathode catalyst layer and the amount of cation exchange ionomer in the conductive layer are preferably essentially the same.

[0036] For example, the overall weight or dimensioning of the catalyst layer and the conductive layer may be accordingly adapted, such that the respective amount of the anion exchange ionomer and the cation exchange ionomer are essentially the same based on the corresponding weight percent in the respective layer. For example, the conductive layer may comprise a larger dimensioning and/or larger overall weight, e.g. by comprising multiple layers, while having a lower weight percent of cation exchange ionomer compared with a respective higher weight percent of anion exchange ionomer, but lower overall weight of the catalyst layer.

[0037] The amount of anion exchange ionomer and cation exchange ionomer may be chosen to provide a predefined hydrophobicity of the overall cathode electrode, wherein the respective ionomers may be provided within the respective layer as a single layer, multiple layers, or as a gradient.

[0038] The term "essentially the same" is to be understood to include absolute amounts or weight percent with a relative difference of up to 10%, but preferably defines a relative difference of up to 5% or even up to 1%.

[0039] The ionomers of the cathode are preferably integrated or embedded in a respective layer, e.g. by spray coating or ink drop application. This has the advantage that the respective ionomer may at least partially penetrate the respective layer and the availability thereof may be improved. Furthermore, this allows a very specific dosing of the respective ionomer, which is particularly advantageous since their loading in the respective layer is a very sensitive parameter. For example, an excess amount of the respective ionomer may block the active catalyst sites by creating a thick diffusion layer whereas a suboptimal amount may limit the extents of the necessary three phase boundaries. The application by drop casting may furthermore facilitate the overall manufacturing of the membrane assembly, e.g. if the anion exchange ionomer layer is also provided by drop casting.

[0040] The weight percent of the anion exchange ionomer and the cation exchange ionomer may each comprise about e.g. 10% while the cation exchange ionomer is preferably present in said different layers to constitute the overall amount or total weight percent.

[0041] The above percentage ranges for the anion exchange ionomer and the cation exchange ionomer, in particular the specific weight percent ranges of the cation exchange ionomer, have been found to be particularly advantageous in terms of controlling the local pH, defining the overall hydrophobicity, and the possibility of blocking potentially salt-forming components. Thereby, CO_2 reduction reactions resulting e.g. in ethylene could be favored. Accordingly, the above preferred percentages enabled a significant improvement in view of the selectivity and durability or stability of the CO_2 reduction provided by the multilayer electrode.

[0042] The conductive layer may comprise a carbon nanoparticle layer comprising a predefined portion of the cation exchange ionomer. The implementation of an additional carbon nanoparticle layer, e.g. as the outer or outermost layer of the gas diffusion layer, has the advantage that an improved surface area for the cation exchange ionomer may be provided, thereby further facilitating the speed of electron transfer. The predefined portion of the cation exchange ionomer may be e.g. between 1 wt. % and 25 wt. % to further support the selective CO_2 reduction reaction and improve the stability of the bipolar gas diffusion electrode.

[0043] The density of the carbon nanoparticle layer is preferably between 0.05 mg/cm^2 and 2 mg/cm^2, more preferably between 0.2 mg/cm^2 and 1 mg/cm^2 or about 0.5 mg/cm^2. Such relative lower density has been found to be advantageous in view of the function of the cation exchange ionomer and/or to enable a predefined level of swelling due to the corresponding hydrophobicity of the cation exchange ionomer.

[0044] Preferably, the weight percent of cation exchange ionomer is essentially the same or essentially continuous within the conductive layer, i.e. for the carbon nanoparticle layer and any optional further layer of the conductive layer. For example, the weight percent may be about 5 wt. % for each layer, wherein essentially the same weight percent in the layers enables an essentially continuous distribution and availability of the cation exchange ionomer in the adjacent layers. Such weight percent may result in an overall amount of cation exchange ionomer essentially corresponding to the overall amount of anion exchange ionomer present in the catalyst layer. Preferably, the weight percent of the anion exchange ionomer present in the catalyst layer may correspond to about 10 wt. % while the weight percent of the cation exchange ionomer may e.g. correspond to 5 wt. % for each of the one or more layers of the conductive layer including the carbon nanoparticle layer(s). In this regard, the dimensioning and/or weight of the catalyst layer and the carbon nanoparticle layer may be adapted, such that the overall amount of anion exchange ionomer and cation exchange ionomer is essentially the same.

[0045] The conductive layer and/or the catalyst layer may also comprise a hydrophobic agent. Such hydrophobic agent may be present in addition to the respective cation exchange ionomer and anion exchange ionomer and may e.g. provide an additional hydrophobicity to achieve an overall predefined hydrophobicity without significantly affecting the bipolarity of the gas diffusion electrode.

[0046] According to a further aspect of the invention, a zero-gap electrochemical cell for CO_2 electrolysis is suggested, comprising an anode catalyst layer, a cation exchange membrane arranged adjacent to the anode catalyst layer, and a membrane assembly according to the invention including a catalyst layer comprising a copper-based cathode catalyst, wherein the membrane assembly is arranged adjacent to the cation exchange membrane.

[0047] The zero-gap electrochemical cell may comprise a gas feed chamber upstream of the cathode catalyst layer, preferably adjacent to a gas diffusion layer to ensure that CO_2 is permeated or conveyed to the cathode catalyst layer in a predefined and controlled manner. Gaseous CO_2 reduction reaction products may also be enriched or be transferred to said gas feed chamber. At the other side of the membrane assembly, i.e. the anode side, an anode catalyst layer is present, which is separated from the membrane assembly by a cation exchange membrane, which together form a half membrane electrode assembly (MEA). Adjacent to the anode catalyst layer at a side opposing the cation exchange membrane, an anolyte flow chamber may be provided.

[0048] By means of the implementation of membrane assembly according to the invention, the zero-gap electrochemical cell hence enables a CO_2 reduction reaction to produce CO_2 reduction reaction products selectively, in particular of ethylene, ethanol, and propanol, as will be shown in view of the examples and Figures further below. Furthermore, the inventive membrane assembly may be efficiently implemented in industrially established zero-gap electrochemical cells. In this regard, the provision of the membrane assembly enables, e.g., that said membrane assembly may be sandwiched between an anode half or membrane electrode assembly of the zero-gap electrochemical cell, i.e. the anode catalyst layer and the cation exchange membrane, and the cathode half, i.e. the cathode gas diffusion electrode, which are commonly produced as separate parts. Therefore, the application of the membrane assembly in existing architectures may be facilitated, achieving a significantly higher level of technology readiness.

[0049] According to a further aspect of the invention, a method for producing a membrane assembly for supporting CO_2 electrolysis in a zero-gap cell electrolyzer is suggested, wherein a mixture of anion exchange ionomer and microparticles and/or nanoparticles comprising or, preferably, being formed of a metal oxide is drop casted, spray coated, or dry pressed to form an anion exchange ionomer layer, wherein the mixture comprises microparticles and/or nanoparticles at a weight percent between 1 wt. % and 50 wt. %. In this manner, a predefined porosity may be achieved, which is dependent on both the type of application or production and the weight percent of the microparticles and/or nanoparticles. Furthermore, the manufacturing method may directly affect the distribution of microparticles and/or nanoparticles and anion exchange ionomer as well as its binding to the adjacent layers, i.e. the cation exchange membrane and the cathode electrode.

[0050] The mixture may be directly applied onto a copper-based cathode catalyst layer by drop casting or alternative processing such as physical vapor deposition, chemical vapor deposition, spray coating. For example, the mixture may be combined with a solvent so as to provide an ink or fluid paste, which may be successively applied to the cathode catalyst layer in order to achieve a predefined height or thickness of the anion exchange ionomer layer. The application may also be performed with different weight percentages of the microparticles and/or nanoparticles, such that e.g. a predefined gradient and/or porosity may be established. By means of the drop casting, for example, an improved control of the application may furthermore be provided.

[0051] Alternatively, the anion exchange ionomer layer may be formed by hot or cold dry pressing the mixture between the cation exchange membrane and the cathode catalyst layer. Accordingly, the anion exchange ionomer layer may be sandwiched between the anode half or half MEA, including the cation exchange membrane and an anode catalyst layer, and a cathode half, including at least the cathode catalyst layer. As described above, this significantly facilitates the implementation of the anion exchange ionomer layer in existing architectures.

[0052] Depending on the respective application of the anion exchange ionomer layer, the dry (hot) pressing is preferably performed at a predefined temperature and for a predefined duration, e.g. between 60°C and 100°C and/or for 1 minute to 10 minutes. This may also be dependent on the thickness of the membrane assembly or anion exchange ionomer layer. By the same token, the applied pressure may be varied depending e.g. on the desired porosity and/or thickness of the anion exchange ionomer layer and may e.g. be between 500 psi and 5000 psi. The applied pressure and/or temperature may furthermore be dependent on the type of ionomer being used and/or the configuration of the anode half and cathode half of a zero-gap electrochemical cell.

Brief description of the drawings

[0053] The present disclosure will be more readily appreciated by reference to the following detailed description when being considered in connection with the accompanying drawings in which:

Figure 1A and 1B are schematic views of a membrane assembly according to the invention;

Figure 2 is a schematic view of an embodiment of a zero-gap electrochemical cell according to the invention;

Figure 3 shows results of faradaic efficiencies for different products obtained with an implemented membrane assembly according to the invention; and

Figure 4 shows results of faradaic efficiencies for different products obtained with an implemented membrane assembly according to another embodiment of the invention.

Detailed description of preferred embodiments

[0054] In the following, the invention will be explained in more detail with reference to the accompanying figures. In the Figures, like elements are denoted by identical reference numerals and repeated description thereof may be omitted in order to avoid redundancies.

[0055] In Figures 1A and 1B, schematic depictions of a membrane assembly 10 according to the invention are shown. In both of the embodiments the type of anion exchange ionomer is the same, preferably, based on or consisting of a polymer named 1H-Imidazole, 1,2,4,5-tetramethyl-, compd. with 1-(chloromethyl)-4-ethenylbenzene polymer with ethenylbenzene. Furthermore, the size or size distribution of the microparticles and/or nanoparticles comprised in the respective anion exchange ionomer layers is the same and both membrane assemblies 10 have been made according to the same method of manufacturing. However, as indicated by the different hatching, the porosity of the membrane layer 10 may be larger in the embodiment depicted in Figure 1A. This is because the weight percent of the microparticles and/or nanoparticles is e.g. about 20 wt. % as opposed to 5 wt. % for the embodiment depicted in Figure 1B.

[0056] By means of the different porosities, the embodiments depicted in Figures 1A and 1B may comprise different efficiencies in the provision of effective three-phase boundaries, since the porosity affects the diffusion of the CO_2 gaseous molecules back to the catalyst layer and/or gas feed chamber.

[0057] While the porosities according to the present examples hence have been predefined by the weight percent of the microparticles and/or nanoparticles in the anion exchange ionomer layer, which is advantageous also in terms of their indirect function as a hydrocarbon production catalyst, it will be understood that other variables, such as the size distribution of the microparticles and/or nanoparticles, the type of anion exchange ionomer being used, and/or the method of manufacturing may also affect the resulting porosity.

[0058] In Figure 2 a schematic view of an embodiment of a zero-gap electrochemical cell 28 according to the invention is shown.

[0059] Accordingly, the zero-gap electrochemical cell 28 is configured for CO_2 electrolysis and accordingly comprises a membrane assembly 10 according to the invention, which is indicated by the corresponding hatching in Figure 2. The membrane assembly 10 is arranged directly adjacent to a cathode catalyst layer 12, together forming a cathode half of a membrane electrode assembly. On the opposing side of the membrane assembly 10, a cation exchange membrane 14 is arranged, such that the membrane assembly 10 is arranged in a sandwich construction between the cathode half and the anode half, these latter two components hence forming the anode half or MEA. The cathode catalyst layer 12 preferably includes a gas diffusion layer and a conductive layer (not shown), such that the membrane assembly may be considered to comprise a gas diffusion electrode. The membrane electrode assembly is bipolar due to the presence of the cation exchange membrane and the anion exchange ionomer layer. Optionally, anion exchange ionomers are present in the cathode catalyst layer and cation exchange ionomers may be present in an optional conductive layer, as described above.

[0060] Adjacent to the cathode catalyst layer 12 and upstream thereof a gas feed chamber 30 is provided, such that CO_2 may be efficiently conveyed to the cathode catalyst layer, e.g. via its gas diffusion layer. On the anode side of the zero-gap electrochemical cell 28, an anode catalyst layer 34 is arranged directly adjacent to the cation exchange membrane 14. On the opposing side of the anode catalyst layer 34, an anolyte flow chamber 38 is provided.

[0061] The zero-gap electrochemical cell 28 hence enables that CO_2 is permeated or conveyed to the cathode catalyst layer 12 in a predefined and controlled manner. By means of the implementation of the membrane assembly 10 according to the invention, the zero-gap electrochemical cell 28 hence enables a CO_2 reduction reaction to produce CO_2 reduction reaction products selectively, in particular of ethylene, ethanol, and propanol, as will be shown in view of the examples in Figures 3 and 4 below. Gaseous CO_2 reduction reaction products may e.g. be enriched or be transferred to the gas feed chamber 30 for collection and optional purification and/or further processing.

[0062] Figure 3 shows results of faradaic efficiencies for different products obtained with an implemented membrane assembly 10 according to the invention. The results have been obtained for a configuration with an anion exchange ionomer layer comprising titanium dioxide particles having a size of about 100 nm and being present at a weight percent in said layer of about 20 wt. %. The membrane assembly 10 used in this experimental setup has furthermore been obtained using dry pressing.

[0063] The electrochemical measurement was performed at a current density of 100 mA/cm2, wherein the product spectrum was assessed after three hours. In Figure 3, the experimental data is depicted as the sum of faradaic efficiency, which has not been normalized to 100% and only corresponds to the gaseous products. With common zero-gap electrochemical cells not even being able to perform an effective CO_2 reduction to hydrocarbons, the provision of the membrane assembly 10 according to the invention enabled the production of ethylene (C_2H_4), as depicted in the left column. While the faradaic efficiency of hydrogen (middle column) still exceeds the level of ethylene, a faradaic efficiency of between 12 and 13 percent could be obtained for ethylene, hence indicating a first-of-its-kind C2H4 producing zero-gap CEM based electrolyzer. The faradaic efficiency of carbon monoxide furthermore did not reach a significant level.

[0064] Similar results were obtained for the experimental setup according to Figure 4, wherein the faradaic efficiency for ethylene was between 12 and 13 percent after a three hour production and for a measurement at the same current density of 100 mA/cm^2. However, for this embodiment, the membrane assembly 10 had been formed by drop-casting. Furthermore, while the same weight percent of titanium dioxide particles had been used, the particles had a size of about 5 μm. In addition, the cathode catalyst layer had been enriched with a conductive layer including or consisting of a carbon nanoparticle layer. Again, the liquid products were not measured and the sum of faradaic efficiency has not been normalized to 100 percent.

[0065] The results indicate that different methods of manufacturing may be implemented with similar results or even moderate improvements for the efficiency of ethylene production. This is likely due to the adjusted level of porosity of the membrane assembly 10 due to the larger particle size and/or alternative method of manufacturing. Furthermore, the inclusion of a conductive layer, e.g. comprising a carbon nanoparticle layer as used in the present example, may furthermore increase the efficiency of selective CO_2 reduction at the cathode catalyst layer.

[0066] It will be obvious for a person skilled in the art that these embodiments and items only depict examples of a plurality of possibilities. Hence, the embodiments shown here should not be understood to form a limitation of these features and configurations. Any possible combination and configuration of the described features can be chosen according to the scope of the invention.

List of reference numerals

[0067]

10	Membrane assembly
12	Cathode catalyst layer or cathode electrode
14	Cation exchange membrane
28	Zero-gap electrochemical cell
30	Gas flow chamber
34	Anode catalyst layer
38	Anolyte flow chamber

Claims

1. A membrane assembly (10) for supporting CO_2 electrolysis in a zero-gap cell electrolyzer, comprising

an anion exchange ionomer layer, wherein said anion exchange ionomer layer comprises microparticles and/nanoparticles at a weight percent between 1 wt. % and 50 wt. %, wherein the microparticles and/or nanoparticles comprise or are formed of a metal oxide.

2. The membrane assembly (10) according to claim 1, wherein the microparticles and/or nanoparticles are present in the anion exchange ionomer layer at a weight percent between 5 wt. % and 35 wt. %, preferably between 15 wt. % and 25 wt. %.

3. The membrane assembly (10) according to claim 1 or 2, wherein the microparticles and/or nanoparticles have a size between 10 nm and 80 pm, said particles preferably having an essentially uniform size.

4. The membrane assembly (10) according to claim 3, wherein the microparticles and/or nanoparticles have a size between 80 nm and 120 nm or between 3 μm and 7 pm, the microparticles and/or nanoparticles preferably being present in the anion exchange ionomer layer at a weight percent between 15 wt. % and 25 wt. %.

5. The membrane assembly (10) according to any of the preceding claims, wherein the microparticles and/or nanoparticles comprise or are formed of titanium dioxide, zirconium dioxide, cerium dioxide, aluminium oxide, yttrium oxide, or silicon dioxide.

6. The membrane assembly (10) according to any of the preceding claims, wherein the anion exchange layer has been formed by drop casting, spray coating, physical vapor deposition, chemical vapor deposition, or dry and hot pressing.

7. The membrane assembly (10) according to any of the preceding claims, further comprising a catalyst layer (12) comprising a copper-based cathode catalyst together forming a membrane electrode assembly, wherein the anion exchange layer preferably has been directly formed on the catalyst layer (12) .

8. The membrane assembly (10) according to claim 6, wherein the catalyst layer (12) comprises a predefined amount of anion exchange ionomer.

9. The membrane assembly (10) according to claim 8, further comprising a conductive layer arranged between the catalyst layer (12) and the anion exchange ionomer layer, wherein the catalyst layer (12) and the conductive layer together form a gas diffusion electrode, and wherein the conductive layer comprises at least one layer comprising a predefined amount of cation exchange ionomer.

10. The membrane assembly (10) according to claim 9, wherein the weight percent of anion exchange ionomer in the catalyst layer (12) is between 1 wt. % and 25 wt. %, , wherein the amount of cation exchange ionomer in the conductive layer preferably corresponds to the amount of anion exchange ionomer.

11. The membrane assembly (10) according to claim 9 or 10, wherein the conductive layer comprises a carbon nanoparticle layer, wherein the weight percent of cation exchange ionomer for said layer is between 1 wt. % and 25 wt. %.

12. A zero-gap electrochemical cell (28) for CO_2 electrolysis, comprising

an anode catalyst layer (34),
a cation exchange membrane (14) arranged adjacent to the anode catalyst layer (34), and
a membrane assembly (10) according to any of claims 6 to 11 arranged adjacent to the cation exchange membrane (14).

13. A method for producing a membrane assembly (10) for supporting CO_2 electrolysis in a zero-gap cell electrolyzer (28), wherein a mixture of anion exchange ionomer and microparticles and/or nanoparticles comprising or being formed of a metal oxide forms an anion exchange ionomer layer by physical vapor deposition, chemical vapor deposition, drop casting, spray coating, or dry pressing , wherein the mixture comprises the microparticles and/or nanoparticles at a weight percent between 1 wt. % and 50 wt.

14. The method according to claim 13, wherein the mixture is applied directly onto a copper-based cathode catalyst layer (12) by drop casting or wherein the anion exchange ionomer layer is formed by hot or cold dry pressing the mixture between the cation exchange membrane (14) and the cathode catalyst layer (12).

15. The method according to claim 13 or 14, wherein the microparticles and/or nanoparticles comprise or are formed of titanium dioxide, zirconium dioxide, cerium dioxide, aluminium oxide, yttrium oxide, or silicon dioxide.

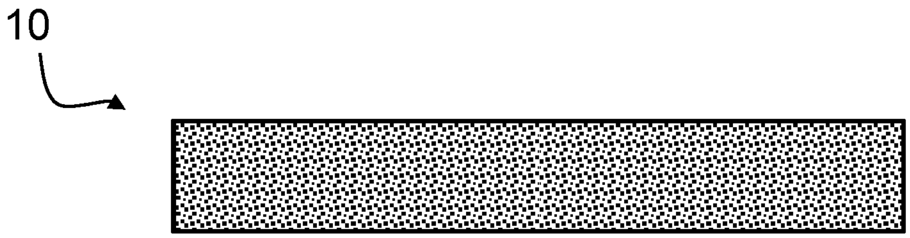


Fig. 1A

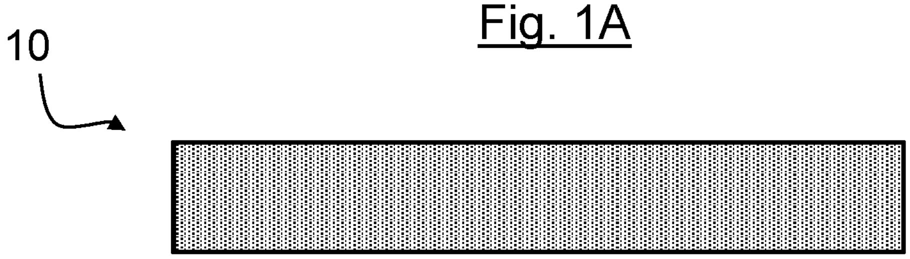


Fig. 1B

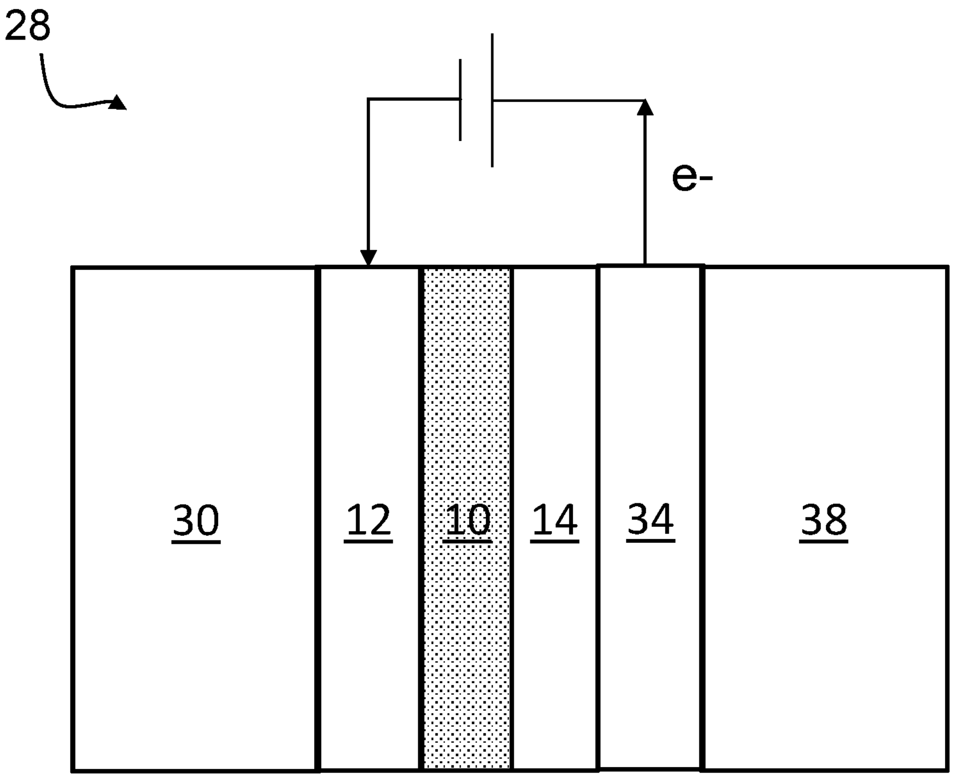
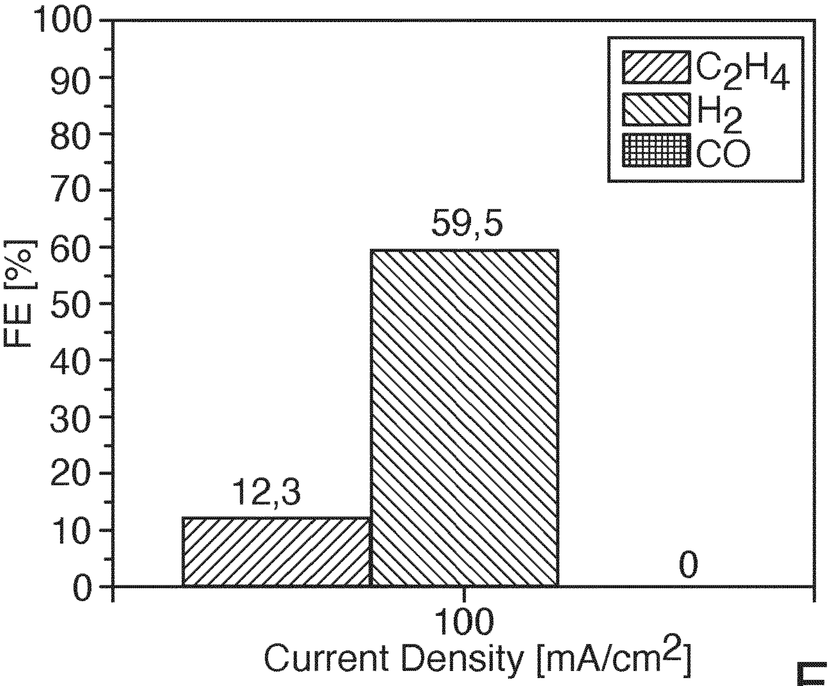


Fig. 2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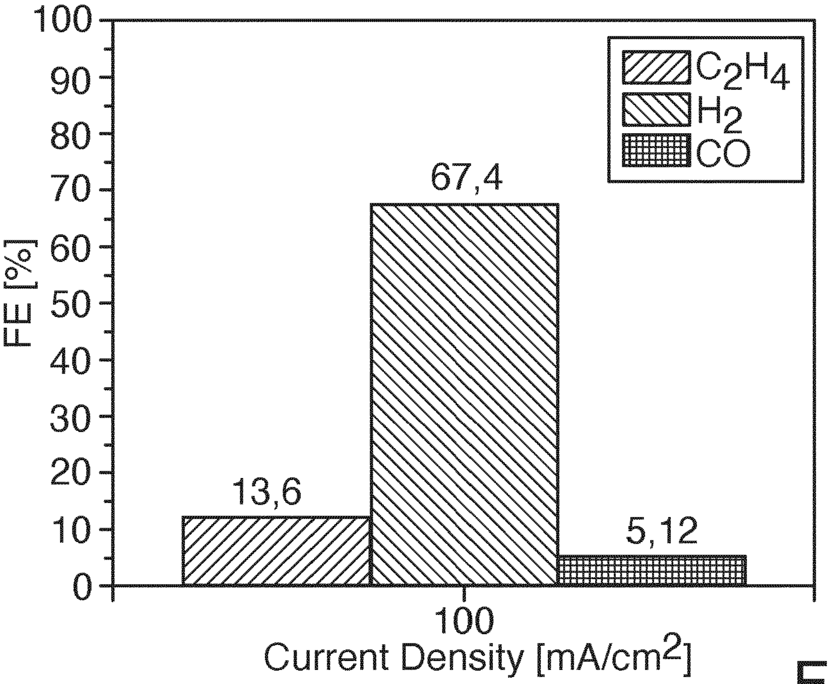
Current Density [mA/cm^2]

Fig. 3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Current Density [mA/cm^2]

Fig. 4

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EUROPEAN SEARCH REPORT

Application Number
EP 23 19 2695

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
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