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(73) Patenthaver: **Siemens Aktiengesellschaft, Werner-von-Siemens-Straße 1, 80333 München, Tyskland**

(72) Opfinder: **KRAUSE, Ralf, Liegnitzerstrasse 6, 91074 Herzogenaurach, Tyskland**
Maltenberger, Anna, Am Köppel 21, 91359 Leutenbach, Tyskland
RELLER, Christian, Driftenweg 2, 32425 Minden, Tyskland
Schmid, Günter, Lange Strasse 13, 91334 Hemhofen, Tyskland
SCHMID, Bernhard, Schwedlerstrasse 37, 91058 Erlangen, Tyskland

(74) Fuldmægtig i Danmark: **Zacco Denmark A/S, Arne Jacobsens Allé 15, 2300 København S, Danmark**

(54) Benævnelse: **Teknik til fremstilling af carbonhydrid-selektive gasdiffusionselektroder på basis af Cu-holdige katalysatorer**

(56) Fremdragne publikationer:
DE-A1- 3 710 168
DE-A1-102005 023 615
RONALD L COOK ET AL: "High Rate Gas Phase Reduction to Ethylene and Methane Using Gas Diffusion Electrodes", JOURNAL OF THE ELECTROCHEMICAL SOCIETY, Bd. 137, Nr. 2, 1. Februar 1990 (1990-02-01), Seiten 607-608, XP055297363, US ISSN: 0013-4651, DOI: 10.1149/1.2086515
KEYOUNG-RAN LEE ET AL: "Reduction of carbon dioxide in 3-dimensional gas diffusion electrodes", KOREAN JOURNAL OF CHEMICAL ENGINEERING, Bd. 16, Nr. 6, 1. November 1999 (1999-11-01), Seiten 829-836, XP055297407, US, KR ISSN: 0256-1115, DOI: 10.1007/BF02698360

Description

The present invention relates to a gas diffusion electrode comprising a preferably copper-containing carrier and a first layer comprising at least copper and at least one binder, wherein the (first) layer comprises hydrophilic and hydrophobic pores and/or channels, further comprising a second layer comprising copper and at least one binder, wherein the second layer is present atop the carrier and the first layer atop the second layer, wherein the content of binder in the first layer is less than in the second layer, to a process for producing such a gas diffusion electrode and to an electrolysis cell comprising such a gas diffusion electrode.

The combustion of fossil fuels currently covers about 80% of global energy demand. These combustion processes emitted about 34 032.7 million metric tons of carbon dioxide (CO_2) globally into the atmosphere in 2011. This release is the simplest way of disposing of large volumes of CO_2 as well (large brown coal power plants exceeding 50 000 t per day).

Discussion about the adverse effects of the greenhouse gas CO_2 on the climate has led to consideration of reutilization of CO_2. In thermodynamic terms, CO_2 is at a very low level and can therefore be reduced again to usable products only with difficulty.

In nature, CO_2 is converted to carbohydrates by photosynthesis. This process, which is divided up into many component steps over time and spatially at the molecular level, is copiable on the industrial scale only with difficulty. The more efficient route at present compared to pure photocatalysis is the electrochemical reduction of the CO_2. As in the case of photosynthesis, in this process, CO_2 is converted to a higher-energy product (such as CO, CH_4, C_2H_4, C1-C4 alcohols etc.) with supply of electrical energy which is preferably obtained from renewable energy sources such as wind or sun. The amount of energy required in this reduction corresponds ideally to the combustion energy of the fuel and should only come from renewable sources or utilize electricity that cannot be accepted from the grid at that moment. However, overproduction of renewable energies is not continuously available, but at present only at periods of strong insolation and/or wind. However, this state of affairs will further intensify in the near future with the further rollout of renewable energy or will level out since the installations will be at different sites.

Not until the 1970s was there an increased level of systematic studies of the electrochemical reduction of CO_2. In spite of many efforts, it has not been possible to date to develop an electrochemical system with which CO_2 could be reduced with long-term stability and in an energetically favorable manner to competitive energy sources with sufficiently high current density and acceptable yield. Owing to the increasing scarcity of fossil raw material and fuel resources and the volatile availability of renewable energy sources, research in CO_2 reduction is moving into the focus of interest to an ever greater degree.

The electrochemical reduction of CO_2 to hydrocarbons, especially to the valuable chemical raw material C_2H_4 (~ €1000/t) has been described in the literature since the 1990s. There has been a significant rise in research activities over the last few years because the availability of excess electrical energy from non-fossil generation sources such as solar or wind is making the storage/utilization of this energy seem viable from an economic point of view.

For electrolysis of CO_2, in general, metals are used as catalysts, some of which are shown by way of example in table 1, taken from Y. Hori, Electrochemical CO_2 reduction on metal electrodes, in: C. Vayenas, et al. (eds.), Modern Aspects of Electrochemistry, Springer, New York, 2008, pp. 89-189.

Table 1 shows the typical Faraday efficiencies (FE) over various metal cathodes. For example, CO_2 is reduced virtually exclusively to CO over Ag, Au, Zn, and to some degree over Pd, Ga, whereas a multitude of hydrocarbons are observed as reduction products over copper. As well as pure metals, metal alloys and also mixtures of metal and co-catalytically active metal oxide are also of interest, since these can increase the selectivity for a particular hydrocarbon. However, the prior art in this regard is not yet very developed.

Table 1: Faraday efficiencies for carbon dioxide over various metal electrodes

Electrode	CH_4	C_2H_4	C_2H_5OH	C_3H_7OH	CO	$HCOO^-$	H_2	Total
Cu	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5
Au	0.0	0.0	0.0	0.0	87.1	0.7	10.2	98.0
Ag	0.0	0.0	0.0	0.0	81.5	0.8	12.4	94.6
Zn	0.0	0.0	0.0	0.0	79.4	6.1	9.9	95.4
Pd	2.9	0.0	0.0	0.0	28.3	2.8	26.2	60.2
Ga	0.0	0.0	0.0	0.0	23.2	0.0	79.0	102.0
Pb	0.0	0.0	0.0	0.0	0.0	97.4	5.0	102.4
Hg	0.0	0.0	0.0	0.0	0.0	99.5	0.0	99.5
In	0.0	0.0	0.0	0.0	2.1	94.9	3.3	100.3
Sn	0.0	0.0	0.0	0.0	7.1	88.4	4.6	100.1
Cd	1.3	0.0	0.0	0.0	13.9	78.4	9.4	103.0
Tl	0.0	0.0	0.0	0.0	0.0	95.1	6.2	101.3
Ni	1.8	0.1	0.0	0.0	0.0	1.4	88.9	92.4
Fe	0.0	0.0	0.0	0.0	0.0	0.0	94.8	94.8
Pt	0.0	0.0	0.0	0.0	0.0	0.1	95.7	95.8
Ti	0.0	0.0	0.0	0.0	0.0	0.0	99.7	99.7

The following reaction equations show, by way of example, reactions at an anode and at a cathode for reduction over a copper cathode. Of particular interest here is the formation of valuable ethylene. Reductions over other metals are analogous to these.

Cathode: $2\ CO_2 + 12\ e^- + 12\ H^+ \rightarrow C_2H_4 + 4\ H_2O$
Anode: $6\ H_2O \rightarrow 3\ O_2 + 12\ H^+ + 12\ e^-$
Overall equation: $2\ CO_2 + 2\ H_2O \rightarrow C_2H_4 + 3\ O_2$

The individual electrode equations show that very complex processes that have not been elucidated in detail to date are proceeding here with, for example, CO or formate intermediates. For each of these intermediates, a particularly preferred position at and/or on the copper cathodes should be necessary. This means that the catalytic activity changes according to the crystallographic orientation of the copper surface, as shown in, for example, Y. Hori, I. Takahashi, O. Koga, N. Hoshi, “Electrochemical reduction of carbon dioxide at various series of copper single crystal electrodes”; Journal of Molecular Catalysis A: Chemical 199 (2003) 39-47; or M. Gattrell, N. Gupta, A. Co, “A review of the aqueous electrochemical reduction of CO_2 to hydrocarbons at copper”; Journal of Electroanalytical Chemistry 594 (2006) 1-19.

In order to be able to provide all these crystallographic surfaces for a high efficiency of ethylene formation at high current density, the electrode must not consist of a smooth sheet, but should be micro- to nanostructured.

The accessibility of such catalytically active sites limits the formation of ethylene to a Faraday efficiency of about 20%, or restricts the achievable current density to +/- 10 mA/cm^2, as described in K. P. Kuhl, E. R. Cave, D. N. Abram, and T. F. Jaramillo, Energy and Environmental Science 5, 7050-7059 (2012).

Furthermore, H. Yano, T. Tanaka, M. Nakayama, K. Ogura, "Selective electrochemical reduction of CO_2 to ethylene at a three-phase interface on copper(I) halide-confined Cu-mesh electrodes in acidic solutions of potassium halides"; Journal of Electroanalytical Chemistry 565 (2004) 287-293, achieved current densities in the region of 100 mA/cm^2, but ethylene here was enriched to a Faraday efficiency (FE) of about 80% in the method of circulating the gaseous substances, and so the "intrinsic" Faraday efficiency of the electrode cannot be determined.

In summary, the current densities of methods known from the prior art are well below the values of relevance for economic utilization.

For the electrochemical reduction of CO_2 to ethylene, it was possible with the aid of copper catalysts deposited in situ to achieve current densities of 170 mA/cm^2 with a Faraday efficiency of > 55% over an electrolysis time of 60 min, as shown in in-house studies. However, in the case of electrodes produced in this way, the selectivity of the electrode can decrease with time, which can lead to an increase in hydrogen production. A change in the selectivity with time can be correlated to structural coarsening of the material, which was also observable, for example, from microscope images. Nano-dendritic copper structures containing both Cu^0 and Cu^I in the form of Cu_2O were identified as a selective catalyst.

Current densities of industrial relevance can be achieved using gas diffusion electrodes (GDE). This is known from the existing prior art, for example, for chloralkali electrolyses operated on the industrial scale. The use of copper-based gas diffusion electrodes in electrolysis cells seems to be advantageous for an energy-efficient conversion of matter from CO_2 to hydrocarbons. One electrode-specific feature of particular interest is the selectivity (Faraday efficiency in %) and the conversion of matter (current density in mA/cm²).

Silver/silver oxide/PTFE (polytetrafluoroethylene)-based gas diffusion electrodes have been used on the industrial scale in recent times for the production of sodium hydroxide solution in existing chloralkali electrolysis processes (oxygen-depolarized electrodes). It was possible to increase the efficiency of the chloralkali electrolysis process by 30-40% by comparison with conventional electrodes. The methodology of catalyst embedding with PTFE is known from a multitude of publications and patterns.

The known embedding methods are divided into three different process routes:

1. Wet methods using a surfactant-stabilized PTFE microemulsion.
2. Wet methods using a surfactant-stabilized Nafion® microemulsion.
3. Dry methods by calendering of premixed catalyst/PTFE mixtures.

In this context, said wet method 1. can have the disadvantages mentioned hereinafter, aside from the fact that examples of gas diffusion electrodes known from the literature contain the catalyst only as an additive and consist mainly of bound conductive charcoal (for high conversions the catalyst loading should be high):
The suspensions or pastes that are usually applied by spraying or bar coating generally have long drying times, which means that continuous production with relatively large electrode areas (of industrial relevance) is not economically possible. Excessively rapid drying leads to cracking, called "mud

cracking”, within the layers applied, which makes the electrode unusable.

The porosity of the layer applied is determined (generated) in the wet-chemical method virtually exclusively by the evaporation of the solvent. This process is highly solvent- or boiling point-dependent and can lead to a high reject rate of the electrodes produced, since the evaporation cannot be assured in a homogeneous manner over the entire area. A further central disadvantage is the use of surface-active substances (surfactants) or thickeners, plasticizers, which are used for stabilization of the particle suspensions since they cannot be removed without residue by the corresponding drying phases or the thermal crosslinking process.

The embedding process 2., wherein Nafion® (perfluorosulfonic acid, PFSA) is used as binder rather than PTFE, likewise has corresponding disadvantages, since a wet-chemical method using appropriate surfactants is being employed here too. Nafion® itself is a hydrophilic ionomer having highly acidic R-HSO_3 groups which can lead to unwanted acid corrosion or partial dissolution of the metal in the case of some catalysts. Nafion®-bound layers additionally have much lower porosity than PTFE-bound layers. The purely hydrophilic properties of Nafion® can likewise be disadvantageous, since Nafion®, owing to its hydrophilic properties, is unsuitable for formation of hydrophobic channels that are advantageous for gas transport within a gas diffusion electrode. Usable electrodes comprising Nafion® should therefore consist of multiple layers in order to be able to implement the essential properties of a GDE. However, multilayer coating processes are not very attractive for economic reasons. Nafion®-based coating processes can additionally lead to unwanted formation of hydrogen.

The drying method 3. is based on a roll calendering process, for example of PTFE/catalyst powder. The corresponding technique can be traced back to EP 0297377 A2, according to which electrodes based on Mn_2O_3 were produced for batteries. DE 3710168A1 makes the first reference to the employment of the drying process with regard to the preparation of metallic electrocatalyst electrodes. The technique was additionally used in patents relating to the production of silver-based (silver(I) or silver(II) oxide) gas diffusion electrodes (oxygen-depolarized electrodes). The patents EP 2444526 A2 and DE 10 2005 023615 A1 mention mixtures having a binder content of 0.5-7%. The carrier used was Ag or nickel meshes having a wire diameter of 0.1-0.3 mm and a mesh size of 0.2-1.2 mm. The powder is applied directly to the mesh before it is supplied to the roll calender. DE 10148599 A1 or EP 0115845 B1 described a similar process in which the powder mixture is first extruded to give a sheet or film which is pressed onto the mesh in a further step.

Owing to the low mechanical stability, the latter method is less suitable than the above-specified one-step process. EP 2410079 A2 describes the one-stage process for production of a silver-based oxygen-depolarized electrode with the addition of metal oxide supplements such as TiO_2, Fe_3O_4, Fe_2O_3, NiO_2, Y_2O_3, Mn_2O_3, Mn_5O_8, WO_3, CeO_2 and spinels such as $CoAl_2O_4$, $Co(AlCr)_2O_4$ and inverse spinels such as $(Co,Ni,Zn)_2(Ti,Al)O_4$, perovskites such as $LaNiO_3$, $ZnFe_2O_4$. Supplements of silicon nitride, boron nitride, TiN, AlN, SiC, TiC, CrC, WC, Cr_3C_2, TiCN have likewise been found to be suitable, and oxides of the ZrO_2, WO_3 type have been identified as being particularly suitable. The materials are explicitly declared as fillers having no catalytic effect. The aim here is explicitly the reduction of the hydrophobic character of the electrode.

DE 10335184 A1 discloses catalysts which can be used as an alternative for oxygen-depolarized electrodes: precious metals, e.g. Pt, Rh, Ir, Re, Pd, precious metal alloys, e.g. Pt-Ru, precious metal compounds, e.g. precious metal sulfides and oxides, and Chevrel phases, e.g. $Mo_4Ru_2Se_8$ or $Mo_4Ru_2S_8$, where these may also contain Pt, Rh, Re, Pd etc.

Known Cu-based gas diffusion electrodes for generation of hydrocarbons on the basis of CO_2 are mentioned, for example, in the papers by R. Cook [J. Electrochem. Soc., vol. 137, no. 2, 1990, p. 607 - 608]. This mentions a wet-chemical method based on a PTFE 30B (suspension)/$Cu(OAc)_2$/Vulkan XC 72 mixture. The method describes how a hydrophobic gas transport layer is applied using three coating cycles, and a catalyst-containing layer using three further coatings. Each step is followed by a drying phase (325°C) with a subsequent static pressing operation (1000-5000 psi). For the electrode obtained, a Faraday efficiency of > 60% and a current density of > 400 mA/cm^2 are reported. However, reproduction experiments which are cited hereinafter as comparative examples demonstrate that the static pressing method described does not lead to stable electrodes. The added Vulkan XC 72 was likewise found to have an adverse effect, and so it was likewise not possible to obtain any hydrocarbons.

K.-R. Lee et al., Korean Journal of Chemical Engineering, vol. 16, 1999, p. 829-836, describes measurements relating to the electrochemical reduction of CO_2 using Cu/PTFE-bonded gas diffusion electrodes, with which the effects of solvent, Cu/C ratio and electrolyte concentration on the characteristics of the reaction products were examined.

DE 101 30 441 A1 discloses a biporous pore system in a gas diffusion electrode, but no two-layer structure. For such a one-layer structure, flooding of the electrode was observed in in-house preliminary tests. A one-layer structure can also be found, for example, in DE 10 2010 031 571 A1. According to DE 101 30 441 A1, a metallic support skeleton is rolled into a catalyst film produced in that document.

US 2013/0280625 A1 discloses a two-layer structure of a gas diffusion electrode, but does not disclose any hydrophobic pores, and discloses only pores in the diffusion layer as hydrophilic layer. A sacrificial material is used in an obligatory manner therein, and is required for formation of pores. However, in-house preliminary tests have shown that this is not appropriate to the aim.

There is thus a need for cathodes for carbon dioxide electrolysis, in which carbon dioxide can be converted effectively to hydrocarbons. In addition, it is an object of the invention to provide a catalyst concept that is not based on in situ copper deposition but provides a copper gas diffusion electrode which can be processed to give an electrode. Moreover, it is an object of the present invention to develop selective electrocatalysts having long-term stability and to embed them into gas diffusion electrodes that can be connected to electrical contacts.

The inventors have found that particularly active and C_2H_4-selective gas diffusion electrodes should satisfy a multitude of parameters required for ethylene formation. There follows a discussion of properties specific to the invention of an electrode of the invention. Furthermore, the inventors have found that specific demands on the catalyst are required in order that the electrode can form ethylene. These criteria are not apparent from the prior art and constitute the basis for the development of hydrocarbon-selective electrodes of this kind.

The following important specific parameters and requirements for a hydrocarbon-selective gas diffusion electrode have been found:

- Good wettability of the electrode surface in order that the aqueous electrolyte or H^+ ions can come into catalyst contact. (H^+ is required for ethylene or alcohols such as ethanol, propanol or glycol.)
- High electrical conductivity of the electrode or of the catalyst and a homogeneous potential distribution across the entire electrode area (potential-dependent product selectivity).
- High chemical and mechanical stability in electrolysis operation (suppression of cracking and corrosion).
- Defined porosity with a suitable ratio between hydrophilic and hydrophobic channels or pores (assurance of availability of CO_2 with simultaneous presence of H^+ ions).

These can be achieved or fulfilled in accordance with the invention.

In a first aspect, the present invention relates to a gas diffusion electrode comprising a preferably copper-containing carrier, preferably in the form of a sheetlike structure, and a first layer comprising at least copper and optionally at least one binder, wherein the first layer comprises hydrophilic and hydrophobic pores and/or channels, further comprising a second layer comprising copper and at least one binder, wherein the second layer is present atop the carrier and the first layer atop the second layer, wherein the content of binder in the first layer is smaller than in the second layer, wherein the second layer comprises 3-30% by weight of binder, preferably 10-30% by weight of binder, further preferably 10-20% by weight of binder, based on the second layer, and the first layer comprises 0-10% by weight of binder, further preferably 0.1-10% by weight of binder, even further preferably 1-10% by weight of binder, particularly preferably 1-7% by weight of binder, in particular preferably 3-7% by weight of binder, based on the first layer.

In a further aspect, the present invention relates to a process for producing a gas diffusion electrode, comprising

- producing a first mixture comprising at least copper and optionally at least one binder,
- producing a second mixture comprising at least copper and at least one binder,
- applying the second mixture comprising at least copper and at least one binder to a preferably copper-containing carrier, preferably in the form of a sheetlike structure,
- applying the first mixture comprising at least copper and optionally at least one binder to the second mixture,
- optionally applying further mixtures to the first mixture, and
- dry rolling the first and second mixtures and optionally further mixtures onto the carrier to form a second layer and a first layer and optionally further layers,

wherein the proportion of binder in the second mixture is 3-30% by weight, preferably 10-30% by weight, further preferably 10-20% by weight, based on the second mixture, and wherein the proportion of binder in the first mixture is 0-10% by weight, preferably 0.1-10% by weight, further preferably 1-10% by weight, even further preferably 1-7% by weight, even further preferably 3-7% by weight, based on the first mixture, wherein the content of binder in the first mixture is smaller than in the second mixture.

The present invention additionally relates, in yet a further aspect, to an electrolysis cell comprising the gas diffusion electrode of the invention.

Further aspects of the present invention can be taken from the dependent claims and the detailed description.

The appended drawings are intended to illustrate embodiments of the present invention and impart further understanding thereof. In conjunction with the description, they serve to elucidate concepts and principles of the invention. Other embodiments and many of the advantages mentioned are apparent with regard to the drawings.

The elements of the drawings are not necessarily shown to scale with respect to one another. Elements, features and components that are identical, have the same function and the same effect are each given the same reference numeral in the figures of the drawings, unless stated otherwise.

Figure 1 shows a schematic diagram of a gas diffusion electrode of the invention with hydrophobic and hydrophilic regions or channels.

Figure 2 shows a schematic diagram of production of a gas diffusion electrode based on an illustrative PTFE-bound catalyst.

Figure 3 shows a schematic of a further embodiment of a gas diffusion electrode of the invention in the form of a multilayer preparation.

Figure 4 to 6 show, in schematic form, illustrative diagrams of a possible construction of an electrolysis cell in one embodiment of the present invention.

Figures 7 and 8 show illustrative configuration forms for a gas distribution chamber downstream of a gas diffusion electrode of the invention in an electrolysis cell of the invention.

Figure 9 shows the results of Faraday efficiencies of the electrolysis cell from comparative example 3.

Figures 10 and 11 show the results of Faraday efficiencies of the electrolysis cell from comparative example 4.

Definitions

"Hydrophobic" in the context of the present invention is understood to mean water-repellent. According to the invention, hydrophobic pores and/or channels are those that repel water. More particularly, hydrophobic properties are associated in accordance with the invention with substances or molecules having nonpolar groups.

"Hydrophilic", by contrast, is understood to mean the ability to interact with water and other polar substances.

In the application, figures are reported in % by weight, unless stated otherwise or apparent from the description.

In a first aspect, the present invention relates to
a gas diffusion electrode comprising
a preferably copper-containing carrier, preferably in the form of a sheetlike structure, and
a first layer comprising at least copper and at least one binder, wherein the (first) layer comprises hydrophilic and hydrophobic pores and/or channels, further comprising a second layer comprising copper and at least one binder, wherein the second layer is present atop the carrier and the first layer

atop the second layer, wherein the content of binder in the first layer is smaller than in the second layer, wherein the second layer comprises 3-30% by weight of binder, preferably 10-30% by weight of binder, further preferably 10-20% by weight of binder, based on the second layer, and the first layer comprises 0-10% by weight of binder, further preferably 0.1-10% by weight of binder, even further preferably 1-10% by weight of binder, particularly preferably 1-7% by weight of binder, in particular preferably 3-7% by weight of binder, based on the first layer.

The second layer, just like the first layer, may comprise hydrophilic and/or hydrophobic pores and/or channels.

What is also described is a gas diffusion electrode comprising a preferably copper-containing carrier, preferably in the form of a sheetlike structure, and
a first layer comprising at least copper and at least one binder, wherein the layer comprises hydrophilic and hydrophobic pores and/or channels.

Figure 1 illustrates the relations between hydrophilic and hydrophobic regions of a GDE, which can achieve a good triphasic liquid/solid/gaseous relationship. In this case, in the electrode, there are hydrophobic channels or regions 1 and hydrophilic channels or regions 2 on the electrolyte side, with catalyst sites 3 of low activity present in the hydrophilic regions 2. In addition, there are inactive catalyst sites 5 on the gas side.

Particularly active catalyst sites 4 are in the triphasic liquid/solid/gaseous region. An ideal GDE thus has maximum penetration of the bulk material by hydrophilic and hydrophobic channels in order to obtain a maximum number of triphasic regions for active catalyst sites. In this respect, it should be ensured in accordance with the invention that the first layer comprises hydrophilic and hydrophobic pores and/or channels. By suitable adjustment of the first layer, it is possible to achieve the effect that a maximum number of active catalyst sites are present in the gas diffusion electrode, which is explained further in the further, especially preferred embodiments and/or the dependent claims.

For hydrocarbon-selective gas diffusion electrodes for carbon dioxide reduction, accordingly, more intrinsic properties are needed than are offered by the known systems. The electrocatalyst and the electrode are accordingly in a close relationship.

The carrier here is not particularly restricted, provided that it is suitable for a gas diffusion electrode and preferably contains copper. For example, it is also possible for parallel wires to form a carrier in the extreme case. In particular embodiments, the carrier is a sheetlike structure, further preferably a mesh, very preferably a copper mesh. This can assure both adequate mechanical stability and functionality as a gas diffusion electrode, for example with regard to a high electrical conductivity. In particular embodiments, the carrier may also be suitable with regard to the electrical conductivity of the first layer. Through the use of copper in the carrier, it is possible to provide a suitable conductivity and to reduce the risk of inward entrainment of unwanted extraneous metals. In preferred embodiments, the carrier therefore consists of copper. A preferred copper-containing carrier, in particular embodiments, is a copper mesh having a mesh size w of $0.3\ \text{mm} < w < 2.0\ \text{mm}$, preferably $0.5\ \text{mm} < w < 1.4\ \text{mm}$, and a wire diameter x of $0.05\ \text{mm} < x < 0.5\ \text{mm}$, preferably $0.1\ \text{mm} \leq x \leq 0.25\ \text{mm}$.

In addition, by virtue of the fact that the first layer comprises copper, it is also possible to assure a high electrical conductivity of the catalyst and, especially in conjunction with a copper mesh, a homogeneous potential distribution across the entire electrode area (potential-dependent product selectivity).

In preferred embodiments, a preferably copper-containing mesh, preferably the copper mesh which is used as carrier, has a mesh size of the carrier between 0.3 and 2.0 mm, preferably between 0.5-1.4 mm, in order to achieve good conductivity and stability.

In particular embodiments, the binder comprises a polymer, for example a hydrophilic and/or hydrophobic polymer, for example a hydrophobic polymer, especially PTFE. This can achieve suitable adjustment of the hydrophobic pores or channels. More particularly, the first layer is produced using PTFE particles having a particle diameter between 5 and 95 µm, preferably between 8 and 70 µm. Suitable PTFE powders include, for example, Dyneon® TF 9205 and Dyneon TF 1750. Suitable binder particles, for example PTFE particles, may, for example, be virtually spherical, for example spherical, and may be produced, for example, by emulsion polymerization. In particular embodiments, the binder particles are free of surface-active substances. The particle size can be determined here, for example, according to ISO 13321 or D4894-98a and may correspond, for example, to the manufacturer data (e.g. TF 9205: mean particle size 8 µm according to ISO 13321; TF 1750: mean particle size 25 µm according to ASTM D4894-98a).

In addition, the first layer comprises at least copper which may, for example, be in the form of metallic copper and/or copper oxide and which functions as catalyst site.

In particular embodiments, the first layer comprises metallic copper in the 0 oxidation state.

In particular embodiments, the first layer comprises copper oxide, especially Cu_2O. The oxide here may contribute to stabilizing the +1 oxidation states of copper and hence to maintaining the selectivity for ethylene with long-term stability. Under electrolysis conditions, it can be reduced to copper.

In particular embodiments, the first layer comprises at least 40 at% (atom percent), preferably at least 50 at% and further preferably at least 60 at% of copper, based on the layer. This can assure both suitable mechanical stability and suitable catalytic activity of this first layer that serves as catalyst layer (CL). In particular embodiments, the copper for production of the gas diffusion electrode of the invention is provided as particles, which are defined further hereinafter.

In addition, the first layer may also comprise further promoters which improve the catalytic activity of the GDE in association with the copper. In particular embodiments, the first layer comprises at least one metal oxide selected from ZrO_2, Al_2O_3, CeO_2, Ce_2O_3, ZnO_2, and MgO; and/or at least one copper-rich intermetallic phase, preferably at least one Cu-rich phase selected from the group of the binary systems Cu-Al, Cu-Zr, Cu-Y, Cu-Hf, CuCe, Cu-Mg and the ternary systems Cu-Y-Al, Cu-Hf-Al, Cu-Zr-Al, Cu-Al-Mg, Cu-Al-Ce with copper contents > 60 at%; and/or copper-containing perovskites and/or defect perovskites and/or $La_{1.85}Sr_{0.15}CuO_{3.930}Cl_{0.053}$ and/or $(La,Sr)_2CuO_4$, preferably $YBa_2Cu_3O_{7-\delta}$ where $0 \leq \delta \leq 1$ (corresponding to $YBa_2Cu_3O_{7-\delta}X_\delta$), $CaCu_3Ti_4O_{12}$, $La_{1.85}Sr_{0.15}CuO_{3.930}Cl_{0.053}$ $(La,Sr)_2CuO_4$. It is stated that the first layer contains at least one metal oxide that preferably has a lower reduction potential than the evolution of ethylene.

Preferred promoters here are the metal oxides.

In particular embodiments, the metal oxide used is water-insoluble, in order that aqueous electrolytes can be used in an electrolysis using the gas diffusion electrode of the invention. By virtue of the redox potential of the metal oxide being lower than that of the evolution of ethylene, it is possible to ensure that ethylene can be prepared from CO_2 by means of the GDE of the invention. In particular embodiments, the oxides are not to be reduced either in a carbon dioxide reduction. Nickel and iron, for example, are unsuitable since hydrogen forms here. Moreover, the metal oxides are preferably not inert, but should preferably constitute hydrophilic reaction sites that can serve for the provision of protons.

The promoters, especially the metal oxide, are able here to promote the function and production of electrocatalysts having long-term stability, in that they stabilize catalytically active copper nanostructures. The structural promoters here can reduce the high surface mobilities of the copper nanostructures and hence reduce their tendency to sinter. The concept originates from heterogeneous catalysis and is used successfully within high-temperature processes.

Promoters used for the electrochemical reduction of CO_2 may especially be the following metal oxides that cannot be reduced to metals within the electrochemical window: ZrO_2 ($E = -2.3$ V), Al_2O_3 ($E = -2.4$ V), CeO_2 ($E = -2.3$ V), MgO ($E = -2.5$). It should be noted here that the oxides mentioned are not added as additives but are part of the catalyst itself. The oxide, as well as its function as a promoter, also fulfills the feature of stabilizing copper in the I oxidation state and additionally also intermediates in the reduction of carbon dioxide, such as CO, C_2H_4 (or OH). There exist many Cu(I) complexes of CO and

C_2H_4, which suggests stability of these postulated intermediates (see, for example, H. Tropsch, W. J. Mattox, J. Am. Chem Soc. 1935, 57, 1102-1103; T. Ogura, Inorg. Chem., 1976, 15 (9), 2301-2303; J. S. Thompson, R. L. Harlow, J. F. Whitney, J. Am. Chem. Soc., 1983, 105 3522-3527; and V. A. K. Adiraju, J. A. Flores, M. Yousufuddin, H. V. Rasika Dias, Organometallics, 2012, 31, 7926-7932).

In particular embodiments, the catalyst has the following inventive features: by contrast with the known heterogeneous Cu/Al_2O_3, Cu/ZrO_2, $Cu/MgO/Al_2O_3$ catalysts used in industry, in particular embodiments, preferably only very copper-rich catalysts having a molar proportion of > 60 at% Cu are used for the electrochemical reduction of CO_2 owing to the electrical conductivity required.

Especially preferred in gas diffusion electrodes of the invention are metal oxide/copper catalyst structures that are produced as follows:

For the production of the metal oxides, the precipitation, in particular embodiments, cannot be effected as frequently described in a pH regime between pH = 5.5-6.5, but can be effected within a range between 8.0-8.5, such that the precursors formed are not hydroxide carbonates similar to malachite ($Cu_2[(OH)_2|CO_3]$), azurite ($Cu_3(CO_3)_2(OH)_2$) or aurichalcite $(Zn,Cu)_5[(OH)_6|(CO_3)_2)]$, but are hydrotalcites ($Cu_6Al_2CO_3(OH)_{16}\cdot 4(H_2O)$), which can be obtained in a greater yield. Likewise suitable are layered double hydroxides (LDHs) having a composition $[M^{z+}_{1-x}M^{3+}_{x}(OH)_2]^{q+}(X^{n-})_{q/n}\cdot yH_2O$ where M^{1+} = Li^+, Na^+, K^+, M^{2+} = Ca^{2+}, Mg^{2+}, Cu^{2+} and M^{3+} = Al, Y, Ti, Hf, Ga. The corresponding precursors can be precipitated under pH control by co-dosage of a metal salt solution and a basic carbonate solution. A particular feature of these materials is the presence of particularly fine copper crystallites having a size of 4-10 nm, which are structurally stabilized by the oxide present.

It is possible to achieve the following effects: the metal oxide, owing to its high specific surface area, can lead to better distribution of the catalyst metal; highly dispersed metal sites can be stabilized by the metal oxide; CO_2 chemisorption can be improved by the metal oxide; copper oxides can be stabilized.

The precipitation can be followed by drying with subsequent calcination in an O_2/Ar gas stream. The oxide precursors produced, according to the method, can also subsequently be reduced directly in an H_2/Ar gas stream, reducing solely the Cu_2O or CuO to Cu and conserving the oxide promoter. The activation step can also be effected by electrochemical means subsequently. In order to improve the electrical conductivity of the layer applied prior to the electrochemical activation, it is also possible to partly mix oxide precursors and activated precursors. In order to be able to increase the underlying conductivity, it is also possible to mix in 0-10% by weight of copper powder in a similar particle size.

It is likewise not ruled out in accordance with the invention that the ready-calendered electrode is subjected to a subsequent calcination/thermal treatment before the electrochemical activation is conducted.

A further means of production of suitable electrocatalysts is based on the approach of the production of copper-rich intermetallic phases, for example Cu_5Zr, $Cu_{10}Zr_7$, $Cu_{51}Zr_{14}$, which can be prepared from the melt. Corresponding ingots can subsequently be ground and fully or partly calcined in an O_2/argon gas stream and converted to the oxide form. Of particular interest are the Cu-rich phases of the binary systems Cu-Al, Cu-Zr, Cu-Y, Cu-Hf, CuCe, Cu-Mg and the corresponding ternary systems having Cu contents > 60 at%: CuYAl, CuHfAl, CuZrAl, CuAlMg, CuAlCe.

Copper-rich phases are known, for example, from E. Kneller, Y. Khan, U. Gorres, *The Alloy System Copper-Zirconium, Part I. Phase Diagram and Structural Relations*, Zeitschrift für Metallkunde 77 (1), p. 43-48, 1986 for Cu-Zr phases, from Braunovic, M.; Konchits, V. V.; Myshkin, N.K.: Electrical contacts, fundamentals, applications and technology; CRC Press 2007 for Cu-Al phases, from Petzoldt, F.; Bergmann, J. P.; Schürer, R.; Schneider, 2013, 67 Metall, 504-507 (see, for example, table 2) for Cu-Al phases, from Landolt-Börnstein - Group IV Physical Chemistry Volume 5d, 1994, p. 1-8 for Cu-Ga phases, and from P. R. Subramanian, D. E. Laughlin, Bulletin of Alloy Phase Diagrams, 1988, 9,1, 51-56 for Cu-Hf phases.

Table 2: Copper-aluminum phases (taken from Petzoldt, F.; Bergmann, J. P.; Schürer, R.; Schneider, 2013, 67 Metall, 504-507)

Phase	Cu [% by wt.]	Al [% by wt.]	Hardness [HV]	Spec. el. resistance [μΩcm]
Cu	100	0	100	1.75
Γ Cu_9Al_4	80	20	1050	14.2
Δ Cu_3Al_2	78	22	180	13.4
ζ_2 Cu_4Al_3	75	25	624	12.2
η_2 CuAl	70	30	648	11.4
Θ $CuAl_2$	55	45	413	8.0
Al	0	100	60	2.9

In the case of these copper-rich intermetallic phases too, the proportion of copper is preferably greater than 40 at%, further preferably greater than 50 at%, more preferably greater than 60 at%.

However, it is not ruled out here that the intermetallic phases also contain nonmetal elements such as oxygen, nitrogen, sulfur, selenium and/or phosphorus, i.e. oxides, sulfides, selenides, nitrides and/or phosphides for example are present. In particular embodiments, the intermetallic phases have been partly oxidized.

In addition, it is possible to use the following copper-containing perovskite structures and/or defect perovskites and/or $La_{1.85}Sr_{0.15}CuO_{3.930}Cl_{0.053}$ and/or $(La,Sr)_2CuO_4$ for electrocatalysts, especially for the formation of hydrocarbons: $YBa_2Cu_3O_{7-\delta}$ where $0 \leq \delta \leq 1$, $CaCu_3Ti_4O_{12}$, $La_{1.85}Sr_{0.15},CuO_{3.930}Cl_{0.053}$, $(La,Sr)_2CuO_4$. In addition, it is not ruled out that mixtures of these materials can be used for electrode preparation or, as required, subsequent calcination or activation steps are conducted.

In particular embodiments, the catalyst particles comprising or consisting of copper, for example copper particles, which are used for production of the GDE of the invention, have a homogeneous particle size between 5 and 80 µm, preferably 10 to 50 µm, further preferably between 30 and 50 µm. In addition, the catalyst particles, in particular embodiments, have a high purity without traces of extraneous metal. By suitable structuring, optionally with the aid of promoters, it is possible to achieve high selectivity and long-term stability.

It is likewise possible for the promoters, for example the metal oxides, to have a corresponding particle size in the production.

The above promoters can additionally achieve or improve the following properties:

- Good wettability of the electrode surface in order that the aqueous electrolyte or H^+ ions can come into catalyst contact. (H^+ is required for ethylene or alcohols such as ethanol, propanol or glycol.)
- High chemical and mechanical stability in electrolysis operation (suppression of cracking and corrosion).
- Defined porosity with a suitable ratio between hydrophilic and hydrophobic channels or pores (assurance of availability of CO_2 with simultaneous presence of H^+ ions).

In order to further adjust the porosity of the electrode, in particular embodiments, it is possible to add copper powder supplements having a particle diameter of 50 to 600 µm, preferably 100 to 450 µm, preferably 100-200 µm. The particle diameter of these supplements, in particular embodiments, is 1/3-1/10 of the total layer thickness of the layer. Rather than Cu, the supplement may also be an inert material such as a metal oxide. This can achieve improved formation of pores or channels.

A gas diffusion electrode of the invention can especially be produced by the production process of the invention as described further down.

In particular embodiments, the first layer comprises less than 5% by weight of, further preferably less than 1% by weight of and even further preferably no charcoal- and/or carbon black-based or -like fillers, for example conductive fillers, based on the layer. It should be noted here that methods known from the literature for GDE production generally refer, both for dry and wet application, to the addition of activated carbons, conductive blacks (such as Vulkan XC72), acetylene black or other charcoals. However, it has been found in accordance with the invention that even traces of charcoals and/or carbon black can distinctly reduce the selectivity of the catalyst with respect to hydrocarbons and promote the unwanted formation of hydrogen.

Moreover, the first layer, in particular embodiments, does not contain any surface-active substances. In particular embodiments, the first and/or second layer additionally do not contain any sacrificial material, for example a sacrificial material having a release temperature of roughly below 275°C, for example below 300°C or below 350°C, and especially any pore former(s) which can typically remain at least partly in the electrode in the case of production of electrodes using such a material.

It has been found by in-house experiments with electrodes produced by wet-chemical means that these residues irreversibly poison a Cu-based catalyst, and so electrodes thus produced did not show any CO_2 reduction to hydrocarbons. The use of surface-active substances or surfactants, for example Triton X, should therefore be avoided in particular embodiments, and so a wet-chemical procedure for the embedding of Cu-based catalysts is unsuitable.

In the first layer of the GDE, the content or proportion of binder, for example PTFE, is 0-10% by weight, further preferably 0.1-10% by weight, even further preferably 1-10% by weight, particularly preferably 1-7% by weight, especially preferably 3-7% by weight, based on the first layer.

The GDE of the invention further comprises a second layer comprising copper and at least one binder, wherein the second layer is present atop the carrier and the first layer atop the second layer, wherein the content of binder in the first layer is smaller than in the second layer, wherein the second layer comprises 3-30% by weight of binder, preferably 10-30% by weight of binder, further preferably 10-20% by weight of binder, based on the second layer. In addition, the second layer may comprise coarser copper or inert material particles, for example having particle diameters of 50 to 700 µm, preferably 100-450 µm, in order to provide a suitable channel or pore structure.

The second layer comprises 3-30% by weight of binder, preferably 10-30% by weight of binder, further preferably 10-20% by weight of binder, preferably > 10% by weight of binder, further preferably > 10% by weight and up to 20% by weight of binder, based on the second layer, and the first layer preferably comprises 0-10% by weight of binder, for example 0.1-10% by weight of binder, preferably 1-10% by weight of binder, further preferably 1-7% by weight of binder, even further preferably 3-7% by weight of binder, based on the first layer. The binder here may be the same binder as in the first layer, for example PTFE. In addition, the particles for production of the second layer, in particular embodiments, may correspond to those in the first layer, but may also be different therefrom. The second layer here is a metal particle layer (MPL) beneath the catalyst layer (CL). Through layering of this kind, it is possible to specifically create highly hydrophobic regions in the MPL and generate a catalyst layer having hydrophilic properties. By virtue of the strongly hydrophobic character of the MPL, it is likewise possible to prevent unwanted penetration of the electrolyte into the gas transport channels, i.e. flooding thereof. Moreover, the second layer forms the contact with the CO_2 and should therefore also be hydrophobic.

In particular embodiments, the second layer partly penetrates the first layer. This can be achieved, for example, by virtue of the process of the invention and enables a good transition between the layers with regard to diffusion.

As well as the second layer, the GDE of the invention may also have further layers, for example atop the first layer and/or on the other side of the carrier.

For production of such a multilayer GDE, for example, it is first possible to apply, by sieving application, a mixture for an MPL based on a highly conductive copper mixture of dendritic copper having particle sizes between 5-100 µm, preferably less than 50 µm, and coarser copper or inert material particles having particle sizes of 100-450 µm, preferably 100-200 µm, having a PTFE content of 3-30% by weight, preferably 20% by weight, in a layer thickness of 0.5 mm for example, to a copper mesh having a mesh size of 1 mm for example (thickness, for example, 0.2-0.6 mm, e.g. 0.4 mm), and to draw it down by means of a frame or coating bar. Corresponding dendritic copper may also be present in the first layer. This may then be followed by further sieving application of the catalyst/PTFE mixture (CL), for example with a PTFE content of 0.1-10% by weight, and smoothing or drawdown, for example by means of a frame of thickness 1 mm, so as to obtain a total layer thickness (Hf) of 1 mm. The layer pre-prepared in this way can then be fed to a calender having a gap width H_0 = 0.4-0.7 mm, preferably 0.5-0.6 mm, and rolled out, so as to obtain a multilayer gas diffusion electrode as shown schematically in figure 3, comprising a copper mesh 8, an MPL 9 and a CL 10. The MPL can achieve better mechanical stability, a further reduction in the penetration of the electrolyte and better conductivity, especially when meshes are used as carriers.

Stepwise production of the GDE by respective sieving application and rolling of each individual layer can lead to lower adhesion between the layers and is therefore less preferred.

In a further aspect, the present invention relates to a process for producing a gas diffusion electrode, comprising

- producing a first mixture comprising at least copper and optionally at least one binder,
- producing a second mixture comprising at least copper and at least one binder,
- applying the second mixture comprising at least copper and at least one binder to a preferably copper-containing carrier, preferably in the form of a sheetlike structure,
- applying the first mixture comprising at least copper and optionally at least one binder to the second mixture,
- optionally applying further mixtures to the first mixture, and
- dry rolling the first and second mixtures and optionally further mixtures onto the carrier to form a second layer and a first layer and optionally further layers,

wherein the proportion of binder in the second mixture is 3-30% by weight of binder, preferably 10-30% by weight, further preferably 10-20% by weight, based on the second mixture, and wherein the proportion of binder in the first mixture is 0-10% by weight, preferably 0.1-10% by weight, further preferably 1-10% by weight, even further preferably 1-7% by weight, even further preferably 3-7% by weight, based on the first mixture, wherein the content of binder in the first mixture is smaller than in the second mixture.

Also described is a process for producing a gas diffusion electrode comprising

- producing a first mixture comprising at least copper and at least one binder,
- applying the first mixture comprising at least copper and optionally at least one binder to a preferably copper-

containing carrier, preferably in the form of a sheetlike structure, and

- dry rolling the first mixture onto the carrier to form a first layer,

wherein the proportion of binder in the mixture is 3-30% by weight, preferably 3-20% by weight, further preferably 3-10% by weight, even further preferably 3-7% by weight, based on the first mixture.

The production of the first and second mixtures or of the first mixture is not particularly restricted here and can be effected in a suitable manner, for example by stirring, dispersing, etc.

When the second mixture is applied, the first mixture may also comprise 0% by weight of binder, i.e. no binder, since binder from the second mixture can diffuse into the first layer that forms from the first mixture in the course of rolling and hence the first layer can also have a content of binder of, for example, at least 0.1% by weight, for example 0.5% by weight, as established in preliminary experiments. In particular embodiments, however, the first mixture in the case of application of 2 or more mixtures comprises binder.

In particular embodiments, the binder comprises a polymer, for example a hydrophilic and/or hydrophobic polymer, for example a hydrophobic polymer, especially PTFE. This can achieve a suitable adjustment of the hydrophobic pores or channels. More particularly, for production of the first layer, PTFE particles having a particle diameter between 5 and 95 µm, preferably between 8 and 70 µm, are used. Suitable PTFE powders include, for example, Dyneon® TF 9205 and Dyneon TF 1750.

In particular embodiments, the copper for the production of the mixture is in the form of particles or catalyst particles, for example including dendritic copper, having a homogeneous particle size between 5 and 80 µm, preferably 10 to 50 µm, further preferably between 30 and 50 µm. In addition, the catalyst particles, in particular embodiments, have a high purity without traces of extraneous metal. By suitable structuring, optionally with the aid of the promoters, as described above, it is possible to achieve high selectivity and long-term stability.

By suitable adjustment of the particle sizes of copper and binder and any further additions such as promoters, it is possible to control the pores and/or channels, i.e. the hydrophobic and hydrophilic pores and/or channels, of the GDE for the passage of gas and/or electrolyte and hence for the catalytic reaction.

In particular embodiments, the first and/or second mixtures do not contain any sacrificial material, for example a sacrificial material having a release temperature of about below 275°C, for example below 300°C or below 350°C, and especially no pore former(s) which can typically remain at least partly in the electrode in the case of production of electrodes using such a material.

In particular embodiments, the first and/or second mixtures are not pasty, for example in the form of inks or pastes, but are in the form of powder mixtures.

The application of a first, second and further mixture(s) is not particularly restricted and can be effected, for example, by scattering application, sieving application, bar coating, etc.

The rolling application is likewise not particularly restricted and can be effected in a suitable manner. Rolling of the mixture or mass (particles) into the structure of the carrier, for example a mesh structure, is explicitly desirable in particular embodiments in order to assure a high mechanical stability of the electrode.

By virtue of the aforementioned two-stage process with formation of a film, this is not the case; the pre-extruded film here lies only on the mesh and has lower adhesion, and also mechanical stability.

As a result, in the case of application of multiple layers too, it is preferable that the mixtures for the layers are applied individually to the carrier and are then rolled collectively, in order to achieve better adhesion between the layers. In this way, the layers may at least partly penetrate one another, for example in a thickness of 1-20 µm.

The mechanical stress on the binder, for example of polymer particles, by the rolling process leads to crosslinking of the powder through the formation of binder channels, for example PTFE fibrils. The attainment of this state is particularly important in order to guarantee suitable porosity or mechanical stability of the electrode. The hydrophobicity can be adjusted via the respective content of polymer or via the physical properties of the catalyst powder. In the case of application of two (or more layers), a suitable binder content in the second mixture has been found to be 10-30% by weight, preferably 10-20% by weight, based on the second mixture, and a suitable proportion of binder in the first mixture to be 0-10% by weight, 0.1-10% by weight, further preferably 1-10% by weight, even further preferably 1-7% by weight, even further preferably 3-7% by weight. In the case of application of just one mixture, a particularly suitable binder content, for example PTFE content, has been found to be 3-30% by weight, preferably 3-20% by weight, further preferably 3-10% by weight and even further preferably 3-7% by weight of binder, based on the first mixture.

The degree of fibrillation of the binder, for example PTFE (structure parameter ζ), correlates directly with the shear rate applied, since the binder, for example a polymer, behaves as a shear-thinning (pseudoplastic) fluid in the rolling application. After the extrusion, the layer obtained, by virtue of the fibrillation, has an elastic character. This change in structure is irreversible, and so this effect cannot be subsequently enhanced by further rolling; instead, the layer, by virtue of the elastic characteristics, is damaged with further action of shear forces. Particularly significant fibrillation can disadvantageously lead to the electrode rolling up on the layer side, and so excessively high contents of binder should be avoided.

For dry rolling application, it is preferable that the water content in the rolling operation corresponds, for example, to the ambient humidity at most. For example, the content of water and solvents in the rolling application is less than 5% by weight, preferably less than 1% by weight and, for example, even 0% by weight.

In particular embodiments, the copper-containing carrier is a copper mesh having a mesh size w of $0.3 \text{ mm} < w < 2.0 \text{ mm}$, preferably $0.5 \text{ mm} < w < 1.4 \text{ mm}$, and a wire diameter x of $0.05 \text{ mm} < x < 0.5 \text{ mm}$, preferably $0.1 \text{ mm} \leq x \leq 0.25 \text{ mm}$. The rolling into a mesh, for example a copper mesh, allows the interstices in the mesh, for example copper mesh, to be effectively bridged by the overlying (for example highly conductive) layer and enables complete 3D contact connection with the electrode. As a result, higher oxide contents are possible.

In particular embodiments, the production of the gas diffusion electrode of the invention is additionally based on the exclusion of charcoal- and/or carbon black-based or -like fillers, for example conductive fillers. The catalyst itself or dendritic copper (formed, for example, through activation of the catalyst) or mixtures of the two serve here as charcoal replacement.

In addition, the method of the invention, in particular embodiments, does not need any surface-active substances/surfactants or thickeners and additives (such as flow improvers) that have been identified as catalyst poisons.

In particular embodiments, the bed height y of the first mixture on the carrier in the application is in the range of $0.3\ \text{mm} < y < 2.0\ \text{mm}$, preferably $0.5\ \text{mm} < y < 1.0\ \text{mm}$. In the case of multiple layers, each layer may have a corresponding bed height y, but the bed heights of all layers preferably do not add up to more than 2.0 mm, preferably to more than 1.5 mm, more preferably to more than 1 mm.

In particular embodiments, the gap width in the rolling application H_0 is the height of the carrier + 40% to 50% of the total bed height Hf of the mixtures of the various layers, for example of the bed height y of the first mixture if it is the only one used.

In particular embodiments, the rolling application is effected by means of a calender.

In particular embodiments, the copper content in the mixture is at least 40 at%, preferably at least 50 at% and further preferably at least 60 at% of copper, based on the mixture.

In particular embodiments, further additions to the mixture include:
at least one metal oxide having a lower reduction potential than the evolution of ethylene, preferably ZrO_2, Al_2O_3, CeO_2, Ce_2O_3, ZnO_2, MgO;
and/or at least one copper-rich intermetallic phase, preferably at least one Cu-rich phase selected from the group of the binary systems Cu-Al, Cu-Zr, Cu-Y, Cu-Hf, CuCe, Cu-Mg and/or the ternary systems Cu-Y-Al, Cu-Hf-Al, Cu-Zr-Al, Cu-Al-Mg, Cu-Al-Ce with copper contents > 60 at%;
and/or at least one metal for formation of a copper-rich metallic phase, preferably Al, Zr, Y, Hf, Ce, Mg, or at least two metals for formation of ternary phases, preferably Y-Al, Hf-Al, Zr-Al, Al-Mg, Al-Ce, such that the copper content is > 60 at%;
and/or copper-containing perovskites and/or defect perovskites and/or $La_{1.85}Sr_{0.15}CuO_{3.930}Cl_{0.053}$ and/or $(La,Sr)_2CuO_4$, preferably $YBa_2Cu_3O_{7-\delta}X_\sigma$, $CaCu_3Ti_4O_{12}$, $La_{1.85}Sr_{0.15}CuO_{3.930}Cl_{0.053}$, $(La,Sr)_2CuO_4$.

The addition of the metal for formation of a copper-rich metallic phase, preferably Al, Zr, Y, Hf, Ce, Mg, or at least two metals for formation of ternary phases, preferably Y-Al, Hf-Al, Zr-Al, Al-Mg, Al-Ce, such that the copper content is > 60 at%, can be effected, for example, in such a way that, in the production of the gas diffusion electrode, intermetallic phases are formed, for example through co-melting and thermal oxidation, and can then be selectively reduced, for example by electrochemical means. However, such co-melting in the mixture is effected here before the binder is added. In such a case, there is thus a sequence in that the metal is first added and fused with copper before the binder and any further substances are added to the mixture.

In particular embodiments, the process of the invention can thus be effected by a calendering process as shown schematically in figure 2. In this case, the catalyst particles 6 and the binder particles 7, for example PTFE particles, are rolled onto the carrier 8, here in the form of a copper mesh, with the aid of a calender 11.

In particular embodiments, the rolling or calendering is conducted at a roller speed between 0.3 and 3 rpm, preferably 0.5-2 rpm. In particular embodiments, the flow rate or an advance rate (of the GDE in length per unit time, for example in the case of calendering) Q is in the range from 0.04 to 0.4 m/min, preferably 0.07 to 0.3 m/min.

In order to further adjust the porosity of the electrode, in particular embodiments, it is possible to add copper powder supplements having a particle diameter of 50 to 600 µm, preferably 100 to 450 µm, further preferably 100 to 200 µm, especially to the second mixture in the case of application of multiple layers. The particle diameter of these supplements, in particular embodiments, is 1/3-1/10 of the total layer thickness of the layer. Rather than copper, the supplement may also be an inert material such as a metal oxide. In this way, it is possible to achieve improved formation of pores or channels.

A process for producing a gas diffusion electrode may thus proceed, for example, as follows: the GDE can be produced using a dry calendering method in which a mixture of a cold-flowing polymer (preferably PTFE) and the respective pre-calcined catalyst powder comprising copper and optionally a promoter is produced in an intensive mixing apparatus or laboratory scale with a knife mill (IKA). The mixing procedure may, for example, follow the following procedure, but is not restricted thereto: grinding/mixing for 30 sec and pause for 15 sec for a total of 6 min, these figures being based, for example, on the knife mill with a total loading of 50 g. After the mixing operation, the mixed powder attains a slightly tacky consistency, with fibrillation here, for example, of the binder, for example PTFE. According to the amount of powder or polymer/chain length chosen, there may also be variation in the mixing time before this state is attained.

The powder mixture obtained is subsequently scattered or sieved onto a copper mesh having a mesh size of > 0.5 mm and < 1.0 mm and a wire diameter of 0.1-0.25 mm in a bed thickness of 1 mm. The powder mixture applied is then drawn down, for example, with a coating bar. This operation can be repeated more than once until a homogeneous layer is obtained. Alternatively, the powder mixture can be pelletized during or after the mixing operation in order to obtain a pourable material, for example having an agglomerate diameter of 0.05 to 0.2 mm.

In order that the powder does not trickle through the mesh, the reverse side of the copper mesh can be sealed with a film subject to no further restriction. The prepared layer is compacted with the aid of a two-roll rolling device (calender). The rolling process itself is characterized in that a reservoir of material forms upstream of the roll. The speed of the roll is between 0.5-2 rpm and the gap width was adjusted to the height of the carrier +40% to 50% of the bed height Hf of the powder, or corresponds virtually to the thickness of the mesh + 0.1-0.2 mm infeed.

In addition, the calender can also be heated. Preference is given to temperatures in the range of 20-200°C, preferably 20-50°C.

The catalyst itself can be processed prior to the application in the calcined state, for example also as a metal oxide precursor, or already in the reduced state. Mixtures of the two forms are possible. This is also true in the case of the intermetallic phases or alloys described, and so these can likewise be used in the oxide form or in the metallic state. Furthermore, it is not ruled out that the calendered electrode can be calcined subsequently, for example at 300-360°C for 5 to 15 min.

It is advantageous for the gas diffusion electrode of the invention, especially in the case of hydrocarbon-selective copper catalyst electrodes, to apply a copper-PTFE base layer as a second layer for better contact connection with nanoscale materials, while simultaneously maintaining a high porosity. The base layer may be characterized by a very high conductivity, for example 7 mohm/cm or more, and preferably has a high porosity, for example of 50-70%, and a hydrophobic character. The binder content, for example PTFE, may be chosen between 3-30% by weight, for example 10-30% by weight. The intermediate copper layer as the second layer may itself be catalytically active in the region of the overlap zone with the catalyst layer as the first layer, and especially serves for better areal electrical connection of the electrocatalyst and can improve the availability of CO_2 owing to the high porosity. With the aid of this method, the required amount of catalyst can be reduced by a factor of 20-30. The corresponding electrocatalyst/binder (e.g. PTFE) mixture can, in a first step, be sieved out onto the reverse side of the current distributor and calendered. It is additionally also possible to apply the 2-layer variant described as a double layer. The binder used, especially PTFE, in particular embodiments, should be treated beforehand in a knife mill in order to achieve fiber formation. Particularly suitable PTFE powders have been found to be, for example, Dyneon® TF 9205 and Dyneon® TF 1750. In order to promote this effect, abrasive hard materials may be mixed in in the range between 0-50% by weight. The following are examples of suitable materials: SiC, B_4C, Al_2O_3 (high-grade corundum), SiO_2 (crushed glass), preferably in a grain size of

50-150 µm. The production of the gas diffusion electrode with a binder-based (e.g. PTFE-based) diffusion barrier is based on multiple layers that cannot be considered in isolation from one another, but preferably have an overlap zone of maximum breadth in the boundary regions, for example of 1-20 µm.

The method of two-layer construction additionally includes the option of dispensing with binder materials as the first layer within the catalyst layer, which means that it is possible to achieve better electrical conductivity. It is likewise possible to process very ductile or brittle powder particles. This is not possible in a single-layer construction. In the case of mechanically sensitive catalysts, it is possible to dispense with the process step of the knife mill, which means that the catalyst remains unchanged since mechanical stress resulting from the mixing operation can be avoided.

Subsequent electrochemical activation of the electrode obtained, in particular embodiments, can optionally be conducted, for example by chemical or electrochemical activation, and is not particularly restricted. An electrochemical activation procedure may lead to penetration of cations of the conductive salt of the electrolyte (e.g. $KHCO_3$, K_2SO_4, $NaHCO_3$, KBr, NaBr) into the hydrophobic GDE channels, thus creating hydrophilic regions. This effect is particularly advantageous and has not been described to date in the literature.

In yet a further aspect, the present invention relates to an electrolysis cell comprising a gas diffusion electrode of the invention, which is preferably used as cathode. In particular embodiments, the gas diffusion electrodes of the invention can be operated specifically in plate electrolyzers.

The further constituents of the electrolysis cell, for instance the anode, optionally one or more membranes, inlet(s) and outlet(s), the voltage source etc., and further optional devices such as cooling or heating units, are not particularly restricted in accordance with the invention, nor are anolytes and/or catholytes that are used in such an electrolysis cell, and the electrolysis cell, in particular embodiments, is used on the cathode side for reduction of carbon dioxide.

In the context of the invention, the configuration of the anode space and the cathode space is likewise not particularly restricted.

Illustrative configurations for an exemplary construction of a typical electrolysis cell and possible anode and cathode spaces are shown in figures 4 to 6.

Electrochemical reduction of CO_2, for example, takes place in an electrolysis cell typically consisting of an anode and a cathode space. Figures 4 to 6 which follow show examples of a possible cell arrangement. For each of these cell arrangements, it is possible to use a gas diffusion electrode of the invention, for example as cathode.

By way of example, the cathode space II in figure 4 is configured such that a catholyte is supplied from the bottom and then leaves the cathode space II at the top. Alternatively, the catholyte can also be supplied from the top, as in the case, for example, of falling-film electrodes. At the anode A which is electrically connected to the cathode K by means of a power source for provision of the voltage for the electrolysis, the oxidation of a substance which is supplied from the bottom, for example, with an anolyte takes place in the anode space I, and the anolyte together with the oxidation product then leaves the anode space. In the 3-chamber construction shown in figure

4, it is additionally possible to convey a reaction gas, for example carbon dioxide, through the gas diffusion electrode into the cathode space II for reduction. Although they are not shown, embodiments with a porous anode are alternatively conceivable. In figure 4, the spaces I and II are separated by a membrane M. By contrast, in the PEM (proton or ion exchange membrane) construction of figure 5, the gas diffusion electrode K and a porous anode A directly adjoin the membrane M, by means of which the anode space I is separated from the cathode space II. The construction in figure 6 corresponds to a mixed form of the construction from figure 4 and the construction from figure 5, wherein a construction with the gas diffusion electrode as shown in figure 4 is provided on the catholyte side, whereas a construction as in figure 5 is provided on the anolyte side. It will be appreciated that mixed forms or other configurations of the electrode spaces shown by way of example are also conceivable. Embodiments without a membrane are additionally conceivable. In particular embodiments, the electrolyte on the cathode side and the electrolyte on the anode side may thus be identical, and the electrolysis cell/electrolysis unit may not need a membrane. However, it is not ruled out that the electrolysis cell in such embodiments has a membrane, although this is associated with additional cost and inconvenience with regard to the membrane and also to the voltage applied. Catholyte and anolyte may also optionally be mixed again outside the electrolysis cell.

Figure 4 to 6 are schematic diagrams. The electrolysis cells from figures 4 to 6 may also be combined to form mixed variants. For example, the anode space may be configured as a PEM half-cell, as in figure 5, while the cathode space consists of a half-cell containing a certain electrolyte volume between membrane and electrode, as shown in figure 4. In particular embodiments, the distance between electrode and membrane is very small or 0 when the membrane is porous and includes a feed of the electrolyte. The membrane may also have a multilayer configuration, such that separate feeds of anolyte and catholyte are enabled. Separation effects are achieved in the case of aqueous electrolytes, for example, through the hydrophobicity of interlayers. Conductivity can nevertheless be assured if conductive groups are integrated into separation layers of this kind. The membrane may be an ion-conducting membrane, or a separator that brings about mechanical separation only and is permeable to cations and anions.

The use of the gas diffusion electrode of the invention makes it possible to construct a three-phase electrode. For example, a gas can be guided from behind toward the electrically active front side of the electrode in order to conduct an electrochemical reaction there. In particular embodiments, there may also merely be flow along the back of the gas diffusion electrode, meaning that a gas such as CO_2 is guided along the back side of the gas diffusion electrode relative to the electrolyte, in which case the gas can penetrate through the pores of the gas diffusion electrode and the product can be removed at the back. Preferably, the gas flow in the case of backflow is the reverse of the electrolyte flow, in order that any liquid forced through can be transported away. In this case too, a gap between the gas diffusion electrode and the membrane as electrolyte reservoir is advantageous.

By virtue of the sufficient porosity of the gas diffusion electrode, two modes of operation are thus possible: one cell variant (a) enables direct active flow of a gas such as CO_2 through the GDE. The products formed are removed from the electrolysis cell through the catholyte outlet and separated from the liquid electrolyte in a downstream phase separator. A disadvantage of this method is the elevated mechanical stress on the GDE and partial or complete forcing of the electrolyte out of the pores. Disadvantages are likewise found to be the elevated occurrence of gas in the electrolyte space and displacement of the electrolyte. For the mode of operation, in addition, a high excess of CO_2 is required. In particular embodiments, only gas diffusion electrodes having a porosity > 70% and elevated mechanical stability are suitable for this mode of operation. The second cell variant describes a mode of operation in which the CO_2 flows within the rear region of the GDE by virtue of an adjusted gas pressure. The gas pressure here should be chosen such that it is equal to the hydrostatic pressure of the electrolyte in the cell, such that no electrolyte is forced through. An essential advantage of the cell variant is a higher conversion of the reaction gas used, for example CO_2, compared to the flow variant.

In order still to prevent passage of electrolyte through the gas diffusion electrode, it is possible to apply a film on the side of the gas diffusion electrode remote from the electrolyte, i.e. on the carrier, for example a mesh, in order to prevent the electrolyte from passing through to the gas. The film here may be provided suitably and is hydrophobic for example.

In particular embodiments, the electrolysis cell has a membrane which separates the cathode space and the anode space of the electrolysis cell in order to prevent mixing of the electrolytes. The membrane here is not particularly restricted, provided that it separates the cathode space and the anode space. More particularly, it essentially prevents passage of the gases that form at the cathode and/or anode through to the anode or cathode space. A preferred membrane is an ion exchange membrane, for example in polymer-based form. A preferred material for an ion exchange membrane is a sulfonated tetrafluoroethylene polymer such as Nafion®, for example Nafion® 115. As well as polymer membranes, it is also possible to use ceramic membranes, for example the polymers that are mentioned in EP 1685892 A1 and/or are laden with zirconia, for example polysulfones.

The material for the anode is likewise not particularly restricted and depends primarily on the reaction desired. Illustrative anode materials include platinum or platinum alloys, palladium or palladium alloys and glassy carbon. Further anode materials are also conductive oxides such as doped or undoped TiO_2, indium tin oxide (ITO), fluorine-doped tin oxide (FTO), aluminum-doped zinc oxide (AZO), iridium oxide, etc. Optionally, these catalytically active compounds can also be applied merely superficially in thin-film methodology, for example on a titanium carrier.

The electrolysis cells from figures 4 to 6 can also be combined to form mixed variants. For example, the anode space can be configured as a proton exchange membrane (PEM) half-cell, while the cathode space consists of a half-cell containing a certain electrolyte volume between membrane and electrode. In the ideal case, the distance between electrode and membrane is very small or 0 when the membrane is porous and includes a feed of the electrolyte. The membrane may also have a multilayer configuration, such that separate feeds of anolyte and catholyte are enabled. Separation effects are achieved in the case of aqueous electrolytes, for example, through the hydrophobicity of interlayers. Conductivity can nevertheless be assured if conductive groups are integrated into separation layers of this kind. The membrane may be an ion-conducting membrane, or a separator that brings about mechanical separation only.

For the distribution of a reaction gas, for example CO_2, behind a gas diffusion electrode of the invention, i.e. on the carrier side, various gas distribution chambers may be provided, of which two illustrative gas distribution chambers are shown in figures 7 and 8. These may be provided in order to further increase the residence time of a reaction gas such as CO_2 and the associated conversion. The gas distributors, especially in the case of a gas diffusion electrode with backflow, can contribute to enhanced mass transfer across the entire electrode area.

Further aspects of the present invention relate to an electrolysis system comprising an electrode of the invention or an electrolysis cell of the invention, and the use of the gas diffusion electrode of the invention in an electrolysis cell or electrolysis system.

The further constituents of the electrolysis system are not restricted any further and can be provided suitably.

The above embodiments, executions and developments can, if viable, be combined with one another as desired. Further possible configurations, developments and implementations of the invention also include combinations that have not been mentioned explicitly of features of the invention that have been described above or are described hereinafter with regard to the working examples. More particularly, the person skilled in the art will also add individual aspects as improvements or supplementations to the respective basic form of the present invention.

The invention is described hereinafter by some illustrative embodiments, but these do not restrict the invention.

Examples

All experiments and also the comparative examples and examples were conducted at a room temperature of about 20°C-25°C, unless stated otherwise.

The pressure in the comparative examples and examples was likewise not varied, but left at room pressure (about 1.013 bar).

The further detailed data are reported for their respective comparative examples or examples.

Comparative examples (negative experiments)

Comparative example 1

In comparative example 1, a multilayer gas diffusion electrode was produced according to the instructions of R. Cook (J. Electrochem. Soc. 1990, 137, 2).

The hydrophobic gas transport layer was produced according to the publication:

2.5 g of Vulkan XC 72 and 2.8 g of Teflon 30B (DuPont) were dispersed in 25 mL of water and applied to a dense copper mesh (100 mesh). The layer applied was dried under air and compressed at 344 bar for 2 min. This procedure was used to produce a total of three layers. This was followed by the compression application of three further catalyst-containing layers having the following mixing ratio: 2.5 g of Vulkan XC 72, 2.61 g of $Cu(OAc)_2*H_2O$, 0.83 g of Teflon 30B, dispersed in 25 mL of H_2O. Each layer applied was dried under air and then compressed at 69 bar. The finished GDE was activated at 324°C in a 10% by volume H_2/Ar gas mixture for 3-4 h and finally compressed once again at 69 bar for 30 sec.

Result: No mechanically stable GDE was obtained over an area of 3.3 cm^2. The drying procedure led to unwanted “mud-cracking” of the layer.

Electrochemical characterization was accomplished using a test setup that corresponds essentially to that of the above-described electrolysis system from figure 6 with flow cells for electrolysis.

In the flow cell, the cathode used was the particular gas diffusion electrode (GDE) with an active area of 3.3 cm², the gas feed rate of carbon dioxide on the cathode side was 50 mL/min, and the electrolyte flow rate on both sides was 130 mL/min. The anode was iridium oxide on a titanium carrier with an active area of 10 cm². The catholyte was a 1 M $KHCO_3$ solution with $KHCO_3$ in a 1 M concentration, and the anolyte was 1 M $KHCO_3$, each in deionized water (18 MΩ), each in an amount of 100 mL, and the temperature was 25°C. In addition, 0.5 M K_2SO_4 was also tried as catholyte, and 2.5 M KOH as anolyte.

In the electrochemical characterization of the GDE, it was not possible to detect any ethylene, but exclusively hydrogen along with small proportions of CO.

Comparative example 2

In a further experiment, the water dispersant was exchanged for ethylene glycol, and comparative example 2 otherwise corresponds to comparative example 1 unless stated otherwise. The use of the higher-boiling dispersant prevented cracking, but it was again not possible to detect any ethylene selectivity.

The following method was used for this purpose:

1.440 g of Vulkan XC 72 (49.5% by weight, 3.2 mg/cm²) were mixed vigorously with 15 mL of ethylene glycol with a disperser within 1 h. Then 2.44 g of a PTFE suspension (Teflon 30B, 50.41% by weight, 3.25 mg/cm²) were added while stirring. The mixture was applied to a copper mesh that corresponded to the one used in comparative example 1 with a coating bar with a thickness of 100 µm and dried under air for at least 24 h. Then the three further catalyst-containing layers were applied as in comparative example 1. Subsequently, the solvent was removed in a drying cabinet at 270°C with a ramp of 10 K/min and isothermal conditions for 1 h. Thereafter, a layer corresponding to the first layer was applied (thickness 100 µm) and the solvent was again removed as above and left to dry under air for 24 h. The electrode was then calcined in an oven at 350°C with a ramp of 10 K/min and isothermal conditions for 2 h and compressed at 5 bar and 160°C for 2 min.

Comparative examples 3.1-3.5

The substrate used in comparative example 3.1 was a commercially available carbon cloth for gas diffusion electrodes (Elat® LT1400W, NuVant) in the form of a microporous layer.

A Nafion® D521 dispersion was applied to this gas diffusion layer as electrocatalyst, which was produced as follows:

0.87 g of $Cu(OAc)_2 \cdot H_2O$ was dissolved in about 1 mL of H_2O. In addition, 1.36 g of Vulkan XC 72 were mixed with 15 mL of ethylene glycol and the dissolved $Cu(OAc)_2$ was added and dispersed for 1 h. Thereafter, 1.5 g of the Nafion® D521 suspension were added and stirred with a glass rod. Thereafter, the mixture was applied to the hydrophobic gas diffusion layer, and dried under air and then in a drying cabinet at 120°C for 2 h. This was followed by calcining in an oven at 250°C with a slope of 10 K/min in an atmosphere of 10% by volume of H_2 in argon, and the calcining was continued under isothermal conditions for a total of 240 min.

The electrode thus obtained was subsequently characterized in terms of its electrochemical properties with a test setup that, apart from the GDE, corresponded to the one from comparative example 1.

In this case, the copper catalyst was provided by reduction of $Cu(OAc)_2 \cdot H_2O$.

In the electrochemical characterization, the results shown in Fig. 9 were achieved, which shows the Faraday efficiency as a function of current density. A Faraday efficiency of 10% is found for ethylene, but this is not stable for a long period.

According to comparative example 3.1, the results shown in table 3 were achieved by variation of the carrier (copper mesh with a mesh size of 0.25 and a wire diameter of 0.14 mm) and of the mixture applied. In comparative example 3.2, in addition, PTFE was used rather than Nafion®.

Table 3: Amounts and results in comparative examples 3.2-3.5

Carrier	Carbon binder [% by wt.]	Nafion® [% by wt.]	Catalyst precursor	Amount of catalyst [mg/cm²]	Catalyst [% by wt.]	Max. FE for C_2H_4 [%]
Cu mesh d = 0.14	**44.5**	**8.94 (PTFE)**	**Cu(OAc)$_2$**	**8.7**	**46.56**	0.8% [500 mA/cm²]
Cu mesh d = 0.14	**44.2**	**16.8**	**Cu(OAc)$_2$**	**14.2**	**39**	1.6% [400 mA/cm²]
Elat® LT1400W	**44.2**	**23.3**	**Cu(OAc)$_2$**	**14.2**	**39**	3.8% [400 mA/cm²]
Elat® LT1400W	**44**	**17.4**	**Cu(OAc)$_2$**	**17.2**	**38.6**	0.2% [600 mA/cm²]

Comparative examples 4.1-4.4

A multilayer gas diffusion electrode was produced as in comparative example 3.1, using a Cu/ZrO_2 catalyst that had been obtained from Cu_8Zr_3 as catalyst. In comparative examples 4.2 and 4.4, the GDE was additionally reduced prior to the measurement, 4.3 relates to an electrochemically activated electrode and 4.4 relates to a hydrogen-activated electrode. The amounts used and results obtained in comparative examples 4.1-4.4 are shown in table 4, with the results additionally shown in figures 10 and 11 for comparative example 4.3. In this context, fig. 10 shows a current series, and fig. 11 a measurement at constant current.

Table 4: Amounts and results in comparative examples 4.1-4.4

Carrier	Carbon binder [% by wt.]	Nafion® [% by wt.]	Catalyst precursor	Amount of catalyst [mg/cm²]	Catalyst [% by wt.]	Max. FE for C_2H_4 [%]
Elat® LT1400W	29.5	1.8	CuO/ZrO_2	68.7	35.5	0.5% [300 mA/cm²]
Elat® LT1400W	29.5	1.8	CuO/ZrO_2	68.7	35.5	0.2% [400 mA/cm²]
Elat® LT1400W	-	2.4	CuO/ZrO_2	97.6	35.5	7.3% [300 mA/cm²]
Elat® LT1400W	-	2.4	CuO/ZrO_2	97.6	35.5	3.3% [300 mA/cm²]

In the case of use of Cu/ZrO_2 as catalyst, a stable product spectrum was obtained over an electrolysis time of 150 min.

In general, the charcoal-based GDEs in comparative examples 1-4 showed elevated Faraday efficiencies for hydrogen. It was concluded from this that carbon in the form of conductive blacks or activated carbons is less suitable for the production of ethylene-selective gas diffusion electrodes.

Comparative example 5

Subsequently, therefore, a GDE based on an aqueous PTFE dispersion with pure copper powder having a grain size of < 45 µm was produced in accordance with the method in Chemical Engineering and Processing 52 (2012) 125-131. In this method, there was absolutely no use of carbon in the form of conductive blacks or activated carbons.

The material used was the following:

PTFE suspension: TF5035R, 58% by weight (Dyneon™),
Surfactant: Triton-100 (Fluka Chemie AG)

Thickener: hydroxyethyl methylcellulose (WalocelMKX 70000 PP 01, Wolff Cellulosics GmbH & Co. KG).

As the starting mixture, a solution that contained 97% by weight of Cu and 3% by weight of PTFE was produced as follows: 150 g of thickener solution (1% by weight of methylcellulose in H_2O), 90.0 g of copper powder, 53.7 g of H_2O and 1.5 g of surfactant were dispersed with an Ultra-Turrax T25 disperser at 13 500 rpm for 5 min (wait for 2 min after dispersing for 1 min).

Thereafter, 4.8 g of PTFE suspension were stirred in with a glass rod and the suspension obtained was applied to a copper mesh as used in comparative example 3.2 at 100°C.

A further GDE was produced on the basis of 0.5% by weight of PTFE by the same procedure. The gas diffusion electrodes produced had very poor wettabilities and, in the case of the 0.5% PTFE content, poor porosities, as determined visually and by microscopy. In addition, it was found that the GDEs contained considerable proportions of the surfactant used, which was identified as a catalyst poison in a controlled experiment. It was likewise not possible to drive out the corresponding catalyst poison Triton X 100 ((p-tert-octylphenoxy)polyethoxyethanol) without residue at temperatures of > 340°C, as confirmed by scanning electron microscopy.

Exclusively hydrogen was obtained with the electrodes produced by this procedure. The experiments made it clear that the use of surfactants is disadvantageous for the formation of ethylene. The method likewise did not lead to homogeneous porosities and, in the case of 3% by weight of PTFE, led to very poor wettability.

Reference example 1

Production of a mixed metal oxide catalyst by coprecipitation:

Illustrative method for Cu/Al_2O_3

An appropriate hydrotalcite precursor of the composition $[Cu_{0.6}Al_{0.4}(OH)_2](CO_3)_{0.4}\cdot mH_2O$ (unknown water content for the freshly precipitated hydrotalcite) is prepared by a coprecipitation. Simultaneously added are a 0.41 M metal salt solution (A) composed of $Cu(NO_3)_2\cdot 3H_2O$ (0.246 mol) and $Al(NO_3)_3\cdot 9H_2O$ (0.164 M) and a hydroxide/carbonate solution (B) composed of 0.3 M NaOH (12 g), 0.045 M $(NH_4)_2CO_3$ (4.32 g), such that the pH is between pH 8 and 8.5.

The addition rate of the metal salt solution was chosen as 120 mL/h. Oswalt ripening was effected for 30 min. Thereafter, the solids were filtered off and washed to neutrality. Thereafter, the precursor was dried at 80°C for 12 h, pulverized and calcined. The calcination step is effected in a tubular furnace having a temperature ramp of $\beta = 2$ K/min up to 300°C with isothermal conditions for 4 h in an argon/oxygen mixture: 20% by volume of O_2/Ar with a flow rate of 200 sccm. The precursor prepared was sieved before use.

Examples: Production of powder-based GDEs

Comparative example 6

A catalyst powder is prepared by coprecipitation of $Cu(NO_3)_2\cdot 3H_2O$ and $ZrO(NO_3)_2\cdot xH_2O$ according to reference example 1 with the respective molar amounts (mol). The pre-calcined catalyst powder (weight 45 g; particle size < 75 µm by sieve analysis) is mixed on the laboratory scale with a knife mill (IKA) (on a large scale, for example, with an intensive mixing apparatus) with PTFE particles (weight 5 g; Dyneon® TF 1750; particle size (d50) = 8 µm according to manufacturer). The mixing procedure follows the following procedure: grinding/mixing for 30 sec and wait for 15 sec for a total of 6 min. This statement is based on the knife mill with total loading 50 g. The mixed powder attains a slightly tacky consistency after the mixing operation. The mixing time before this state is attained may also vary according to the amount of powder or the polymer chosen or the chain length. The powder mixture obtained is subsequently applied by scattering or sieving to a copper mesh having a mesh size of > 0.5 mm and < 1.0 mm and a wire diameter of 0.1-0.25 mm in a bed thickness of 1 mm.

In order that the powder does not trickle through the mesh, the reverse side of the copper mesh can be sealed with a film subject to no further restriction. The prepared layer is compacted with the aid of a two-roll rolling device (calender). The rolling process itself is characterized in that a reservoir of material forms upstream of the roll. The speed of the roll is between 0.5-2 rpm and the gap width was adjusted to the height of the carrier +40% to 50% of the bed height Hf of the powder, or corresponds virtually to the thickness of the mesh + 0.1-0.2 mm infeed.

The gas diffusion electrode obtained is activated in an electrolysis bath in a 1 M $KHCO_3$ solution at a current density of 15 mA/cm^2 for 6 h.

Comparative example 7

Dendritic copper powder (45 g; particle size < 45 µm, determined by sieving with appropriate mesh size (45 µm)) is mixed with 5 g of PTFE in an IKA knife mill by the procedure described in comparative example 6, and processed under the same conditions to give a GDE. After activation, the GDE described gave a Faraday efficiency of 16% at 170 mA/cm^2, which remained constant over the measurement time of about 90 min.

Comparative example 8

$Cu_{10}Zr_7$ is calcined in a tubular furnace with a temperature ramp of β = 2 K/min up to 600°C with isothermal conditions for 4 h in an argon/oxygen mixture (20% by volume of O_2/Ar with a flow rate of 200 sccm). The oxide precursor prepared, prior to use, is ground in a planetary ball mill (Pulverisette) for 3 min and subsequently sieved (particle size < 75 µm). 45 g of the catalyst obtained are mixed with 5 g of PTFE in an IKA knife mill by the procedure described in comparative example 6 and processed under the same conditions to give a GDE.

The GDEs from comparative examples 6 to 8 can be used in an electrolysis cell as described above or hereinafter, for example as cathode with which CO_2 can be reduced.

Example 1

Production of a 2-layer electrode

Copper powder with a particle diameter of 100-200 µm and PTFE TF 1750 Dyneon were mixed in an IKA A10 knife mill for 6 min (grinding for 15 sec, wait for 30 sec). The powder layer was then sieved off and graded by means of a template of thickness 0.5 mm to form a base layer. This was followed by extrusion with a 2-roll calender with a roll separation of 0.5 mm. Thereafter, a catalyst layer was applied by sieving application, for example in each case analogously to comparative examples 6 to 8, through a 0.2 mm frame, and extrusion was again effected with a 2-roll calender with a roll separation of 0.35 mm. The result was a highly porous base layer with a porosity of > 70%, good mechanical stability and very good conductivity at 5 mohm/cm. It was possible to use catalysts with a copper content of 40% by weight.

Preferably, the catalysts had a purity above the commercially available materials or quality standards, as in the example as well. This was detectable by means of (surface-sensitive) XPS. SEM/EDX mapping analyses likewise did not indicate any impurities at all in the hydrophobic base layer.

It was additionally found that a copper content of > 70% is advantageous in order to enable a low electrical resistance of the catalyst. The effect of the binder (PTFE) content with respect to the carrier oxide is much smaller in terms of the effect on conductivity.

Illustrative construction of a typical electrolysis cell:
The electrochemical reduction of the CO_2 takes place in an electrolysis cell which typically consists of an anode space and a cathode space. Figures 4 to 6 show examples of a possible cell arrangement. The concept presented hereinafter is applicable to each of these cell arrangements.

The electrolysis cells from figures 4 to 6 can also be joined to form mixed variants. For example, the anode space can be executed as a proton exchange membrane (PEM) half-cell, while the cathode space consists of a half-cell containing a certain electrolyte volume between membrane and electrode. In the ideal case, the distance between electrode and membrane is very small or 0 when the membrane is porous and includes a feed of the electrolyte. The membrane may also have a multilayer configuration, such that separate feeds of anolyte and catholyte are enabled. Separation effects are achieved in the case of aqueous electrolytes, for example, through the hydrophobicity of interlayers. Conductivity can nevertheless be assured if conductive groups are integrated into separation layers of this kind. The membrane may be an ion-conducting membrane, or a separator that brings about mechanical separation only.

The present invention provides the possibility of producing ethylene-selective, dimensionally stable gas diffusion electrodes based on catalyst powder. This technique constitutes the basis for the production of electrodes on a larger scale, which can achieve current densities of > 170 mA/cm^2 according to the mode of operation. All the methods known to date for production of ethylene-selective copper electrodes are unsuitable for scaleup or are not dimensionally stable. Gas diffusion electrodes of the invention, by contrast, can be obtained by suitable adjustment of a rolling process, especially a calendering process.

It is possible in accordance with the invention to obtain highly electrically conductive, especially metal oxide-stabilized, copper catalysts with copper nanostructures that enable oxidation cycling between Cu(I)/Cu(0).

In particular embodiments, the production of the gas diffusion electrode of the invention is additionally based on the exclusion of conductive fillers based on charcoals or carbon blacks. The charcoal substitute used here is the catalyst itself or dendritic copper or mixtures of the two. Moreover, the method of the invention, in particular embodiments, does not need surface-active substances/surfactants or thickeners and additives (such as flow improvers) which have been identified as catalyst poisons.

Patentkrav

1. Gasdiffusionselektrode, omfattende
en, foretrukket kobberholdig, bærer, foretrukket i form af en fladestruktur, og et første lag omfattende i det mindste kobber og eventuelt mindst et bindemiddel, hvor det første lag omfatter hydrofile og hydrofobe porer og/eller kanaler, yderligere omfattende et andet lag omfattende kobber og mindst et bindemiddel, hvor det andet lag befinder sig på bæreren og det første lag på det andet lag, hvor indholdet af bindemiddel i det første lag er mindre end i det andet lag, hvor det andet lag omfatter 3 - 30 vægt-% bindemiddel, foretrukket 10 - 30 vægt-% bindemiddel, mere foretrukket 10 - 20 vægt-% bindemiddel, beregnet i forhold til det andet lag, og det første lag omfatter 0 - 10 vægt-% bindemiddel, mere foretrukket 0,1 - 10 vægt-% bindemiddel, endnu mere foretrukket 1 - 10 vægt-% bindemiddel, særligt foretrukket 1 - 7 vægt-% bindemiddel, især foretrukket 3 - 7 vægt-% bindemiddel, beregnet i forhold til det første lag.

2. Gasdiffusionselektrode ifølge krav 1, hvor det første lag ikke omfatter noget carbon- og/eller kønrøg-baseret fyldstof.

3. Gasdiffusionselektrode ifølge krav 1 eller 2, hvor det første lag ikke indeholder nogen overfladeaktive stoffer.

4. Gasdiffusionselektrode ifølge et af de foregående krav, hvor det første lag omfatter mindst 40 at-%, foretrukket mindst 50 at-%, mere foretrukket mindst 60 at-% kobber, beregnet i forhold til laget.

5. Gasdiffusionselektrode ifølge et af de foregående krav, hvor den kobberholdige bærer er et kobbernet.

6. Gasdiffusionselektrode ifølge et af de foregående krav, hvor det første lag indeholder mindst en metaloxid, som er udvalgt blandt ZrO_2, Al_2O_3, CeO_2, Ce_2O_3, ZnO_2 og MgO;
og/eller hvor det første lag indeholder mindst en kobberrig intermetallisk fase, foretrukket mindst en Cu-rig fase, som er udvalgt fra gruppen af de binære systemer Cu-Al, Cu-Zr, Cu-Y, Cu-Hf, CuCe, Cu-Mg og de ternære systemer Cu-Y-Al, Cu-Hf-Al, Cu-Zr-Al, Cu-Al-Mg, Cu-Al-Ce med Cu-indhold > 60 at-%;

og/eller hvor det første lag indeholder kobberholdige perowskiter og/eller defekt-perowskiter og/eller $La_{1,85}Sr_{0,15}CuO_{3,930}Cl_{0,053}$ og/eller $(La,Sr)_2CuO_4$, foretrukket $YBa_2Cu_3O_{7-\delta}$, hvor $0 \leq \delta \leq 1$, $CaCu_3Ti_4O_{12}$, $La_{1,85}Sr_{0,15}CuO_{3,930}Cl_{0,053}$, og/eller $(La, Sr)_2CuO_4$.

7. Gasdiffusionselektrode ifølge et af de foregående krav, hvor det andet lag delvist trænger igennem det første lag.

8. Fremgangsmåde til fremstilling af en gasdiffusionselektrode, omfattende
- fremstilling af en første blanding omfattende i det mindste kobber og eventuelt mindst et bindemiddel,
- fremstilling af en anden blanding omfattende i det mindste kobber og mindst et bindemiddel,
- påføring af den anden blanding omfattende i det mindste kobber og mindst et bindemiddel på en, foretrukket kobberholdig, bærer, foretrukket i form af en fladestruktur,
- påføring af den første blanding omfattende i det mindste kobber og eventuelt mindst et bindemiddel på den anden blanding,
- eventuel påføring af yderligere blandinger på den første blanding, og
- tør opvalsning af den anden og første blanding og eventuelt yderligere blandinger på bæreren med henblik på at danne et andet og et første lag og eventuelt yderligere lag,

hvor andelen af bindemiddel i den anden blanding udgør 3 - 30 vægt-% bindemiddel, foretrukket 10 - 30 vægt-%, mere foretrukket 10 - 20 vægt-%, beregnet i forhold til den anden blanding,
og hvor andelen af bindemiddel i den første blanding udgør 0 - 10 vægt-%, foretrukket 0,1 - 10 vægt-%, mere foretrukket 1 - 10 vægt-%, endnu mere foretrukket 1 - 7 vægt-%, endnu mere foretrukket 3 - 7 vægt-%, beregnet i forhold til den første blanding, hvor indholdet af bindemiddel i den første blanding er mindre end i den anden blanding.

9. Fremgangsmåde ifølge krav 8, hvor den kobberholdige bærer er et kobbernet med en maskevidde w på 0,3 mm < w < 2,0 mm, foretrukket 0,5 mm < w < 1,0 mm og en tråddiameter x på 0,05 mm < x < 0,5 mm, foretrukket 0,1 mm ≤ x ≤ 0,25 mm.

10. Fremgangsmåde ifølge et af kravene 8 og 9, hvor fyldhøjden y af den første blanding på bæreren ved påføringen ligger i området 0,3 mm $< y <$ 2,0 mm, foretrukket 0,5 mm $\leq y \leq$ 1,0 mm.

11. Fremgangsmåde ifølge et af de foregående fremgangsmådekrav, hvor spaltebredden ved opvalsningen H_0 er højden af bæreren + 40 % til 50 % af den samlede fyldhøjde Hf af den første blanding og eventuelt yderligere blandinger.

12. Fremgangsmåde ifølge et af de foregående fremgangsmådekrav, hvor opvalsningen foregår ved hjælp af en kalander.

13. Fremgangsmåde ifølge et af de foregående fremgangsmådekrav, hvor kobberindholdet i den første blanding er mindst 40 at-%, foretrukket mindst 50 at-%, mere foretrukket mindst 60 at-% kobber, beregnet i forhold til blandingen.

14. Fremgangsmåde ifølge et af de foregående fremgangsmådekrav, hvor der til den første blanding yderligere tilsættes mindst et metaloxid, som har et mindre reduktionspotentiale end ethylenudviklingen, foretrukket ZrO_2, Al_2O_3, CeO_2, Ce_2O_3, ZnO_2, MgO;
og/eller hvor der til den første blanding yderligere tilsættes mindst en kobberrig intermetallisk fase, foretrukket mindst en Cu-rig fase udvalgt fra de binære systemer Cu-Al, Cu-Zr, Cu-Y, Cu-Hf, CuCe, Cu-Mg og/eller de ternære systemer Cu-Y-Al, Cu-Hf-Al, Cu-Zr-Al, Cu-Al-Mg, Cu-Al-Ce med Cu-indhold > 60 at-%;
og/eller hvor der til den første blanding tilsættes mindst et metal til dannelse af en kobberrig metallisk fase, foretrukket Al, Zr, Y, Hf, Ce, Mg, eller mindst to metaller til dannelse af ternære faser, foretrukket Y-Al, Hf-Al, Zr-Al, Al-Mg, Al-Ce, således at Cu-indholdet er > 60 at-%;
og/eller hvor der til den første blanding tilsættes kobberholdige perowskiter og/eller defekt-perowskiter og/eller $La_{1,85}Sr_{0,15}CuO_{3,930}Cl_{0,053}$ og/eller $(La,Sr)_2CuO_4$, foretrukket $YBa_2Cu_3O_{7-\delta}$, hvor $0 \leq \delta \leq 1$, $CaCu_3Ti_4O_{12}$, $La_{1,85}Sr_{0,15}CuO_{3,930}Cl_{0,053}$, og/eller $(La,Sr)_2CuO_4$.

15. Elektrolysecelle, omfattende en gasdiffusionselektrode ifølge et af kravene 1 til 7.

FIG 1

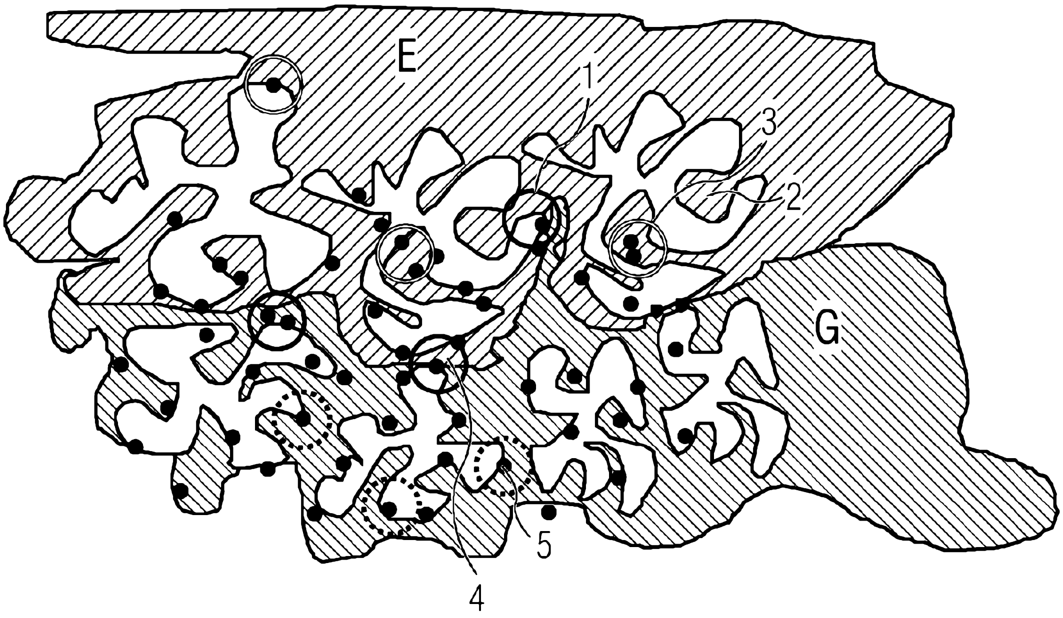
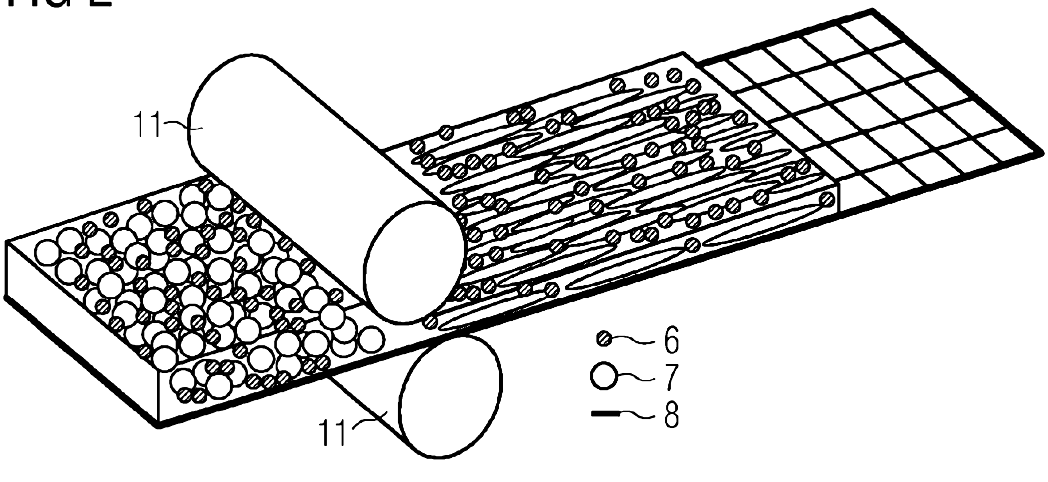


FIG 2



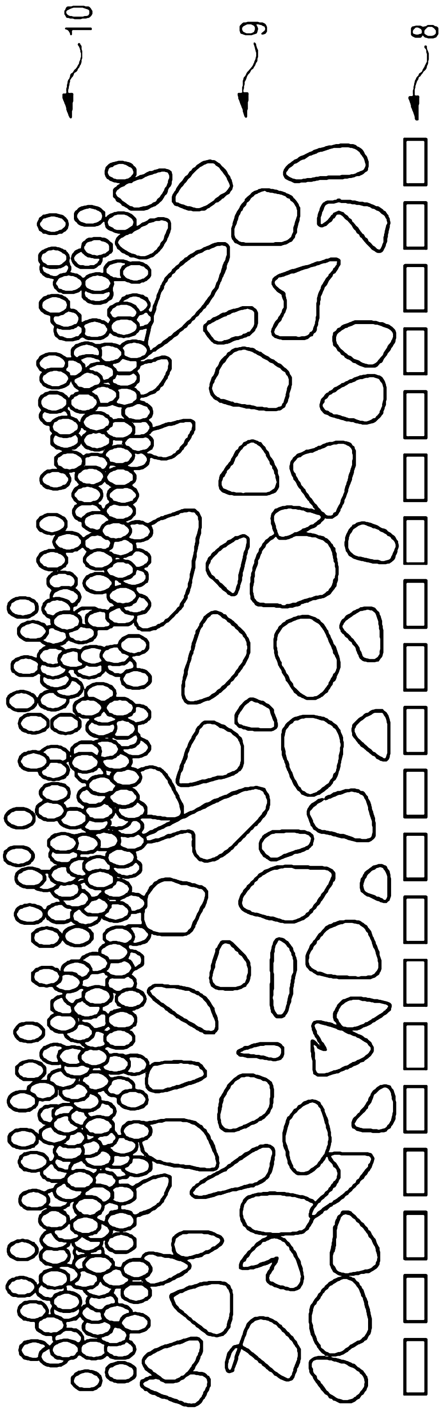
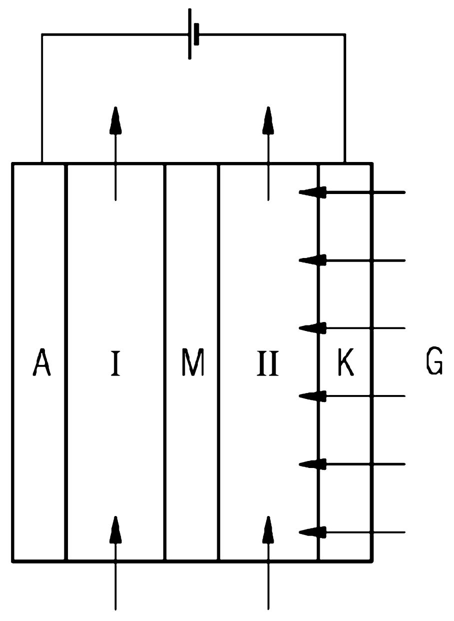


FIG 3

FIG 4



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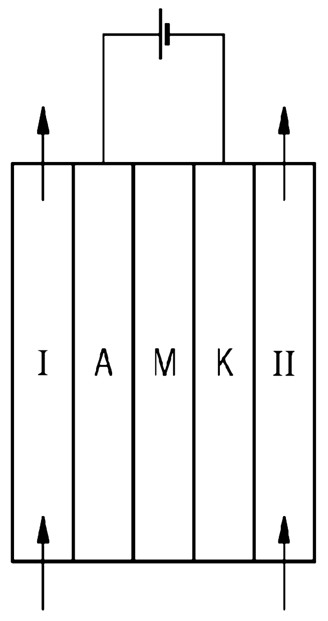

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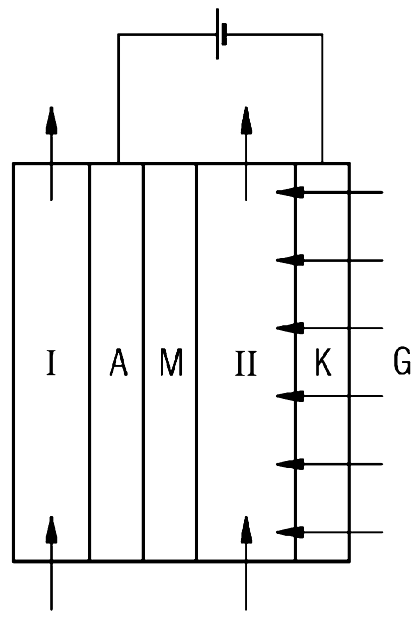


FIG 7

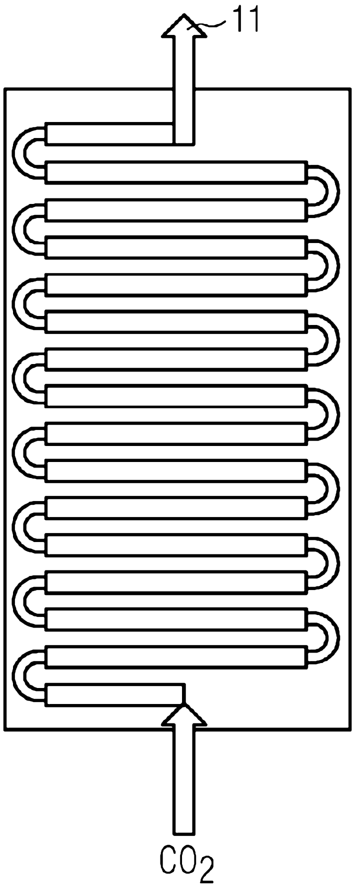


FIG 8

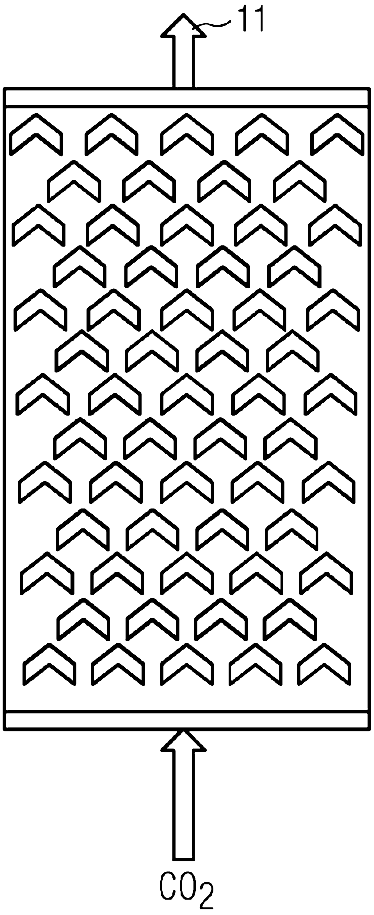


FIG 9

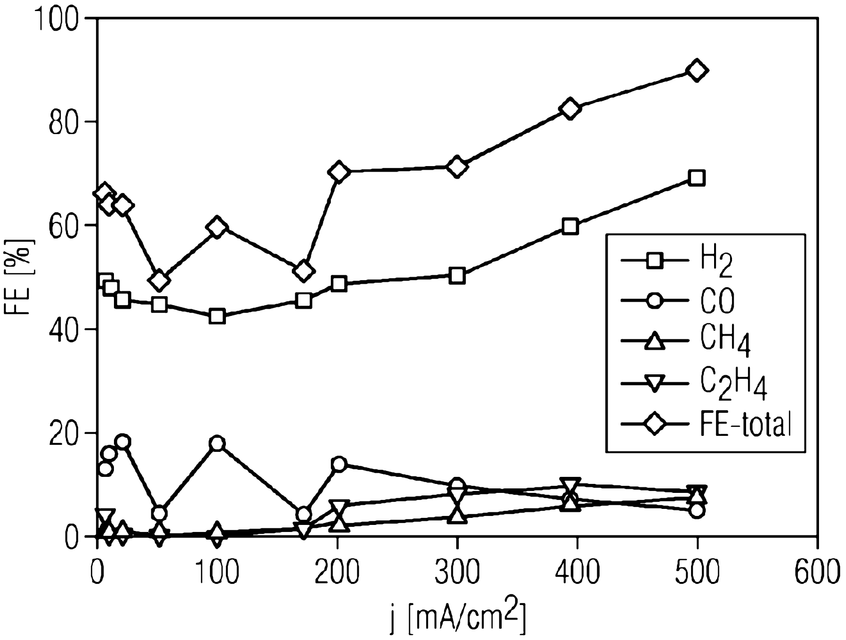
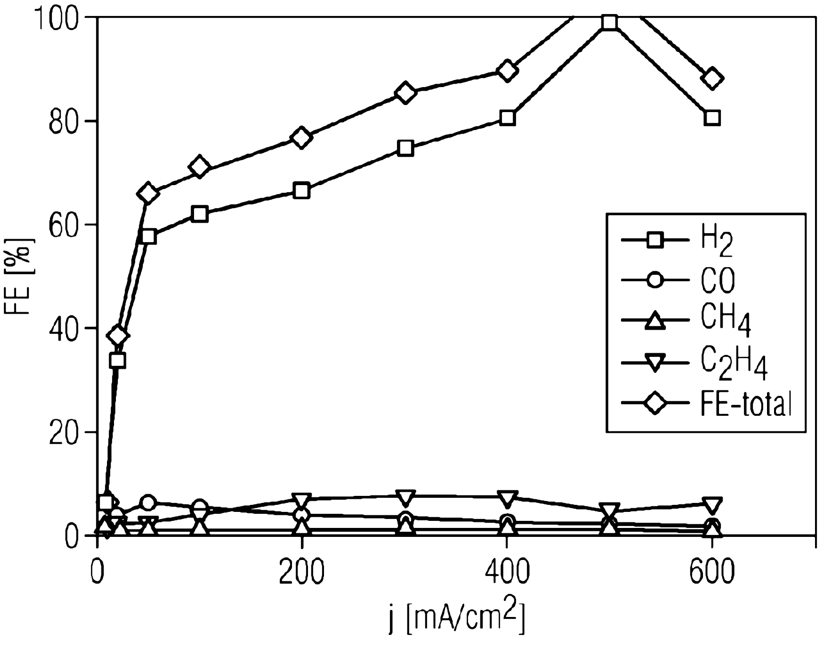

100
80
60
40
20
0
FE [%]
0
100
200
300
400
500
600
j [mA/cm^2]
H$_2$
CO
CH$_4$
C$_2$H$_4$
FE-total

FIG 10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80
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40
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FE [%]
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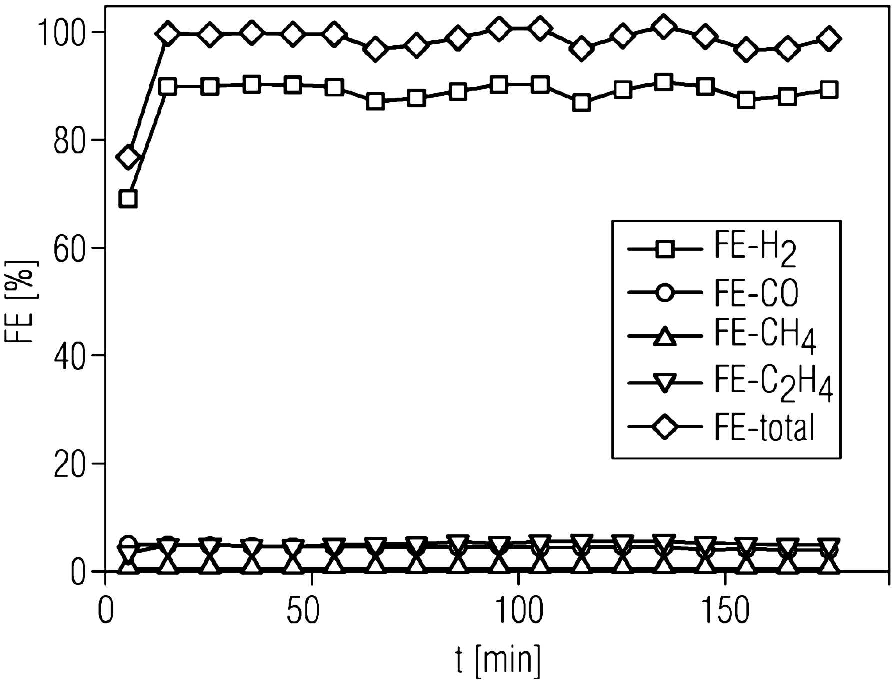
j [mA/cm^2]
H$_2$
CO
CH$_4$
C$_2$H$_4$
FE-total

FIG 11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80
60
40
20
0
FE [%]
0
50
100
150
t [min]
FE-H_2
FE-CO
FE-CH_4
FE-C_2H_4
FE-total