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(54) **METHOD AND DEVICE FOR THE ELECTROCHEMICAL UTILIZATION OF CARBON DIOXIDE**

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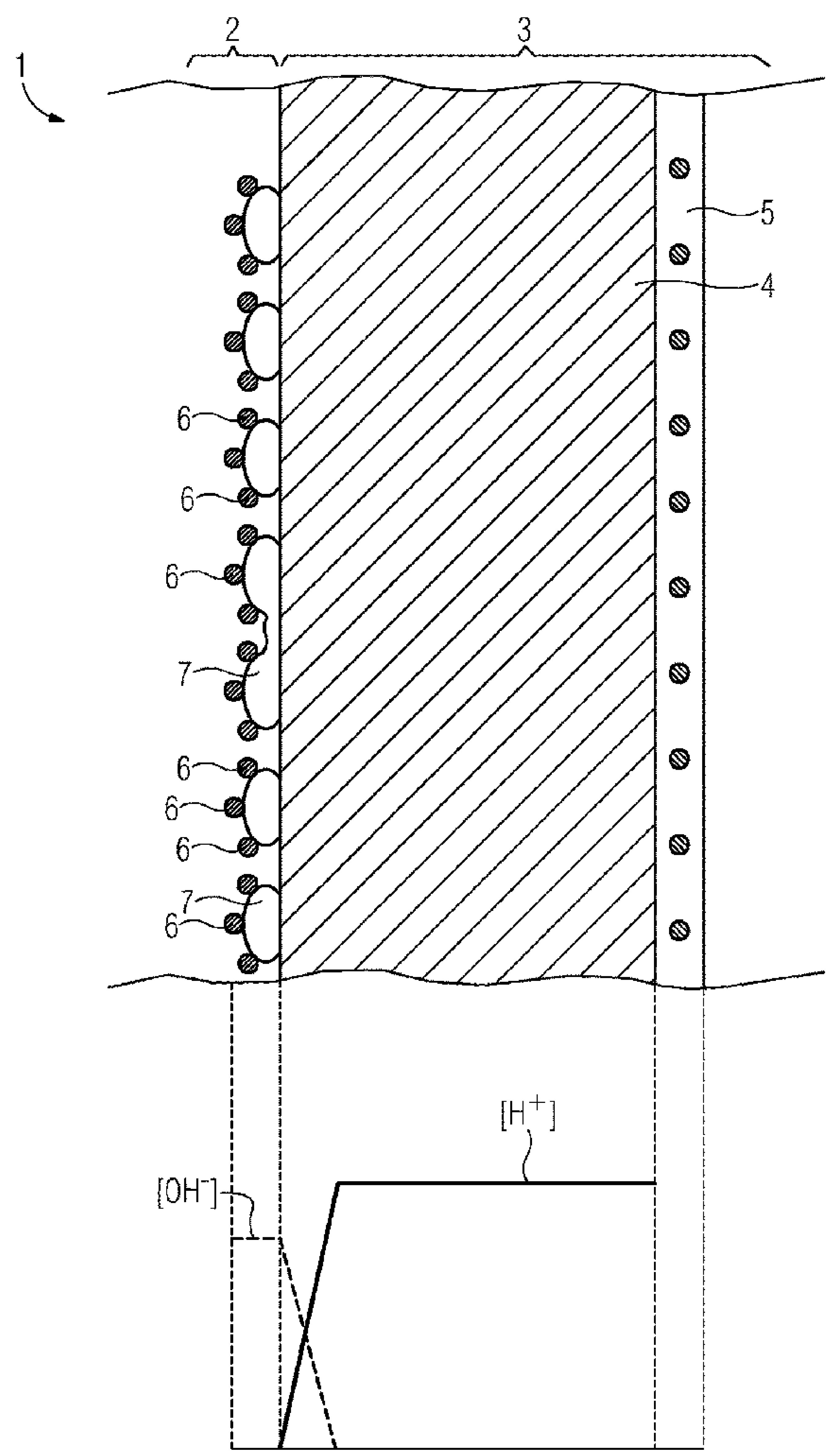
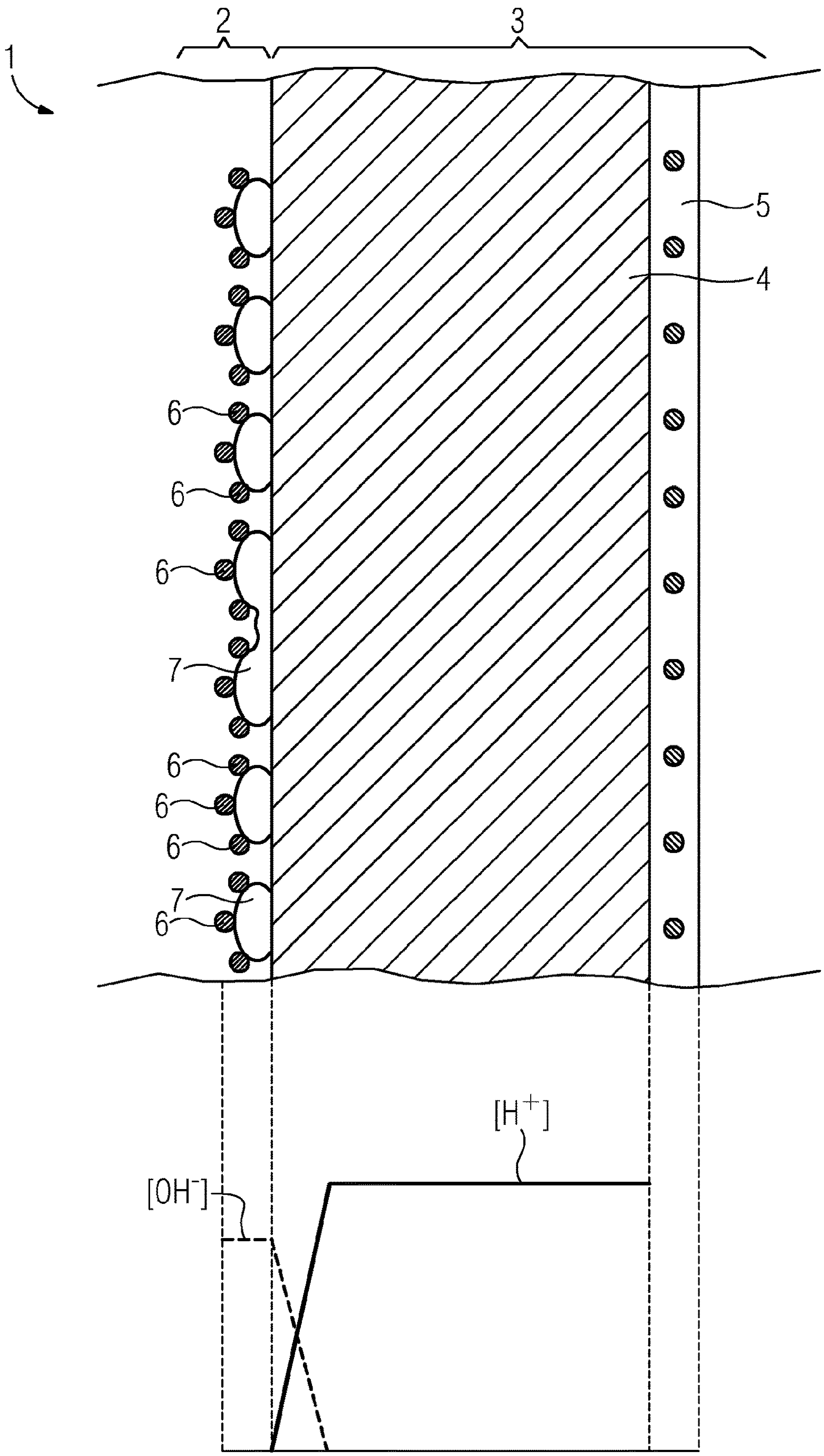
(57) **ABSTRACT**

Various embodiments may include an electrolyzer for electrochemical utilization of carbon dioxide comprising: an electrolysis cell defining an anode space and a cathode space; an anode; a cathode; a first cation-permeable membrane disposed between the anode space and the cathode space; and a layer comprising an anion-selective polymer disposed between the first membrane and the cathode. The anode directly adjoins the first cation-permeable membrane and the layer covers at least part of the cathode but not all of the cathode.

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METHOD AND DEVICE FOR THE ELECTROCHEMICAL UTILIZATION OF CARBON DIOXIDE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a U.S. National Stage Application of International Application No. PCT/EP2017/061185 filed May 10, 2017, which designates the United States of America, and claims priority to DE Application No. 10 2016 209 447.5 filed May 31, 2016, the contents of which are hereby incorporated by reference in their entirety.

TECHNICAL FIELD

[0002] The present disclosure relates to electrochemistry. Various embodiments may include methods and electrolyzer for electrochemical utilization of carbon dioxide.

BACKGROUND

[0003] The demand for power varies significantly over the course of the day. There is also variation in the generation of power, with an increasing proportion of power from renewable energies during the course of the day. In order to be able to compensate for a surplus of power in periods with a lot of sun and strong wind when demand for power is low, controllable power plants or storage means are required to store this energy. One of the solutions currently being contemplated is the conversion of electrical energy to products of value, especially platform chemicals or synthesis gas. One possible technique for conversion of electrical energy to products of value is electrolysis.

[0004] The electrolysis of water to hydrogen and oxygen is known. But the electrolysis of carbon dioxide to give products of value, such as carbon monoxide, ethylene, or formic acid has also been a subject of research for some years, and there are efforts to develop an electrochemical system that can convert a carbon dioxide stream in accordance with economic interests.

[0005] Some electrolysis units include a low-temperature electrolyzer in which carbon dioxide as reactant gas is converted in a cathode space with the aid of a gas diffusion electrode. The carbon dioxide is reduced to products of value at a cathode of the electrochemical cell, and water is oxidized to oxygen at an anode. Owing to diffusion limitations at the cathode, use of an aqueous electrolyte can result not only in the formation of products of value but also disadvantageously in the formation of hydrogen, since the water in the aqueous electrolyte is likewise electrolyzed.

[0006] The formation of hydrogen is promoted when a proton-conducting membrane is in direct contact with the cathode. In some alternatives, there is an aqueous electrolyte-filled gap between the proton-conducting membrane and the cathode. However, it is not possible to use pure water as electrolyte since the conductivity of water would be too low and would result in a high voltage drop in the gap. The use of a mineral acid, especially of diluent sulfuric acid, also leads to unwanted formation of hydrogen since these acids increase the proton concentration at the cathode.

[0007] In some systems, the conductivity of the electrolyte within the gap is therefore increased by adding a base or a conductive salt. It is possible for hydroxide ions to form in the non-acidic medium in the reduction of carbon dioxide at the cathode. These form hydrogencarbonate or carbonate with further carbon dioxide. Together with the cations of the base or the cations of the conductive salt, this may lead to sparingly soluble substances that precipitate out within the electrolysis cell in solid form. This may lead to a shortened lifetime of the electrolysis cell. Fundamentally, a gap in the electrolysis cell may create a drop in voltage across the cell; a rise in the energy required by the electrolysis cell leads to a drop in efficiency.

[0008] A further means of suppressing the unwanted formation of hydrogen is the choice of a suitable cathode material. The cathode material should show maximum overvoltage for the formation of hydrogen. However, metals of this kind are frequently toxic or lead to adverse environmental effects. Suitable metals are cadmium, mercury, and thallium. Moreover, the selection of these metals as cathode material restricts the selection of products of value: the product of value which is prepared in the carbon dioxide electrolysis cell depends to a crucial degree on the reaction mechanism, which is in turn affected by the cathode material as a central factor.

SUMMARY

[0009] The teachings of the present disclosure may be embodied in an electrolyzer and/or a method of operating an electrolyzer, in which the formation of hydrogen is reduced and the efficiency is simultaneously increased.

[0010] As an example, some embodiments may include an electrolyzer for electrochemical utilization of carbon dioxide, comprising at least one electrolysis cell (**1**), where the electrolysis cell (**1**) comprises an anode space (**3**) having an anode (**5**) and a cathode space (**2**) having a cathode (**6**), a first cation-permeable membrane (**4**) is disposed between the anode space (**3**) and the cathode space (**2**) and the anode (**5**) directly adjoins the first membrane (**4**), characterized in that a layer (**7**) comprising an anion-selective polymer is disposed between the first membrane (**4**) and the cathode (**6**) and where the layer (**7**) covers the cathode (**6**) at least partly but not completely.

[0011] In some embodiments, a surface area of the first membrane (**4**) within a range from 20% to 85% is covered by the layer.

[0012] In some embodiments, the cathode (**6**) comprises at least one of the elements silver, copper, lead, indium, tin or zinc.

[0013] In some embodiments, the cathode (**6**) comprises a gas diffusion electrode.

[0014] As another example, some embodiments may include a method of operating an electrolyzer for electrochemical utilization of carbon dioxide, comprising the following steps: providing an electrolyzer having at least one electrolysis cell (**1**), where the electrolysis cell (**1**) comprises an anode space (**3**) having an anode (**5**) and a cathode space (**2**) having a cathode (**6**), and a first cation-permeable membrane (**4**) is disposed between the anode space (**3**) and the cathode space (**2**) and the anode (**5**) directly adjoins the first membrane (**4**), characterized in that a layer (**7**) comprising an anion-selective polymer is disposed between the first membrane (**4**) and the cathode (**6**), decomposing carbon dioxide to give a product at the cathode (**6**) in the cathode space (**2**), forming carbonate or hydrogencarbonate from unconverted carbon dioxide and hydroxide ions (OH^-) at the cathode (**6**), transporting hydrogen ions (H^+) from the anode (**5**) through the first membrane (**4**), reacting the hydrogen ions (H^+) and the carbonate or hydrogencarbonate to give carbon dioxide and water in a contact region of the layer (**7**) and the first membrane (**4**), and releasing the carbon dioxide through flow channels or pores in the layer (**7**).

[0015] In some embodiments, the electrolyzer is operated with pure water.

[0016] In some embodiments, at least one of the products carbon monoxide, ethylene or formic acid is produced.

[0017] As another example, some embodiments may include a method of manufacturing an electrolyzer having an anion-selective polymer layer (**7**) at the cathode (**6**), wherein the cathode (**6**) is impregnated with the anion-selective polymer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] Further configurations and further features of the invention are elucidated in detail by the FIGURE which follows.

[0019] The FIGURE shows an electrolysis cell having a cathode, an anion-selective polymer layer and an anode. In addition, the FIGURE shows concentration profiles of protons and hydroxide ions for operation with pure water.

DETAILED DESCRIPTION

[0020] In some embodiments, an electrolyzer for electrochemical utilization of carbon dioxide comprises at least one electrolysis cell, where the electrolysis cell comprises an anode space having an anode and a cathode space having a cathode. A first cation-permeable membrane is disposed between the anode space and the cathode space and the anode directly adjoins the first membrane. According to the invention, a layer comprising an anion-selective polymer is disposed between the first membrane and the cathode.

[0021] In some embodiments, a method for operation of an electrolyzer for electrochemical utilization of carbon dioxide, the following steps are conducted: firstly, an electrolyzer having at least one electrolysis cell is provided, where the electrolysis cell comprises an anode space having an anode and a cathode space having a cathode. A first cation-permeable membrane is disposed between the anode space and the cathode space. The anode directly adjoins the first membrane.

[0022] In some embodiments, a layer comprising an anion-selective polymer is disposed between the first membrane and the cathode. This layer serves as a contact mediator between the first membrane and the cathode. As the next step, carbon dioxide is decomposed to give a product at the cathode in the cathode space. Carbonate or hydrogencarbonate is then formed from unconverted carbon dioxide and hydroxide ions at the cathode. At the same time, hydrogen ions are transported from the anode through the first membrane. The hydrogen ions and the carbonate or hydrogencarbonate then react in a contact region of the layer and the first membrane to give carbon dioxide and water. The carbon dioxide can be released from the electrolysis cell through flow channels or pores in the layer.

[0023] In some embodiments, the effect of the anion-selective polymer in the first layer is to exclude cations and allow only anions to pass through. This is implemented by means of immobilized positively charged ions. Typically, quaternary amines NH_4^+ are immobilized. The total charge of the anion-selective layer is compensated for by mobile anions dissolved in the aqueous phase of the electrolysis cell, especially hydroxide ions, but also hydrogencarbonate ions.

[0024] In some embodiments, the anion-selective layer prevents hydrogen protons in particular from getting to the cathode. The unwanted formation of hydrogen is thus advantageously avoided. Moreover, it is possible to choose the cathode material in a flexible manner since the anion-selective layer already stops hydrogen protons from getting directly to the cathode. In some embodiments, the selection of a cathode material depends on the product of value desired. The cation-permeable membrane may be implemented by means of immobilized negative charges, especially by deprotonated sulfonic acid groups. The charge is then balanced by protons or other dissolved cations, if present.

[0025] An unwanted but unavoidable effect in the utilization of the anion-selective layer is that some of the carbon dioxide supplied reacts with the hydroxide ions at the cathode to give carbonate or hydrogencarbonate. This hydrogencarbonate or carbonate can be transported through the anion-selective layer. In contact with the hydrogen protons that can pass through the cation-permeable membrane, the hydrogencarbonate or carbonate reacts to give carbon dioxide.

[0026] In some embodiments, the layer covers the cathode at least partly but not completely. The carbon dioxide thus formed can escape from the electrolysis cell. The partial coverage of the layer is effected in an island-like manner on the membrane. In some embodiments, the polymer layer can cover the cathode in a coherent manner when sufficient porous structures are present in the layer to allow the carbon dioxide to escape from the electrolysis cell. The carbon dioxide thus formed then passes into the cathode space, where it can in turn be converted to product of value.

[0027] In some embodiments, the yield of carbon dioxide in the electrolysis cell is thus increased. In addition, in the case of operation of the electrolysis cell with pure water, an excess of water forms at the contact site of the anion-selective layer with the cation-selective membrane as a result of occurrence of neutralization reactions of the carbon dioxide formed from hydrogencarbonate and protons. This water formed can escape in the cathode space direction, and hence ensures good and homogeneous moistening.

[0028] In some embodiments, the surface of the first membrane is covered by the layer within a range from 20% up to 85%. Within this range, it is assured that the polymer layer will separate the cathode from the cation-permeable membrane, but there are simultaneously channels or pores present to allow the carbon dioxide and water to escape. This range relates to layers comprising a nonporous polymer. In some embodiments, the layer comprises a porous polymer. In this case, the surface of the first membrane may be up to 100% covered, i.e. completely covered, by the layer since carbon dioxide and water can then escape through pores.

[0029] In some embodiments, the cathode comprises at least one of the elements silver, copper, lead, indium, tin or zinc. The selection of the cathode material enables a selection of the products of value formed in the electrolysis cell. More particularly, carbon monoxide can be prepared when a silver cathode is used, ethylene when a copper catalyst is used, and formic acid when a lead cathode is used.

[0030] In some embodiments, the cathode comprises a gas diffusion electrode. A gas diffusion electrode is understood to mean a porous catalyst structure of good electron conductivity that has been partly wetted by the adjoining membrane material. Remaining pore spaces are open to the gas side in the gas diffusion electrode.

[0031] The gas diffusion electrode advantageously enables the diffusing-in of carbon dioxide and the diffusing of the carbon monoxide out of the electrode, and ensures that the yield of carbon monoxide is advantageously elevated as a result.

[0032] In some embodiments, the carbon dioxide released, as well as the water, is guided back into the cathode space as reactant. In some embodiments, when a gas diffusion electrode is used, the carbon dioxide released can diffuse through the gas diffusion electrode back into the cathode space. Recycling via an external conduit is additionally possible, but is not absolutely necessary.

[0033] In some embodiments, the electrolyzer is operated with pure water. Pure water is understood to mean water having a conductivity of less than 1 mS/cm. In some embodiments, the use of pure water avoids precipitation of salts or carbonates during the electrolysis. In some embodiments, this prolongs the lifetime and increases the efficiency of the electrolysis cell.

[0034] Some embodiments include a method for production of an electrolyzer having an anion-selective polymer layer at the cathode, the cathode is impregnated with anion-selective polymer. In some embodiments, the impregnation is effected via a dipping method or by spraying the cathode with anion-selective polymer.

[0035] The FIGURE shows a working example of an electrolyzer with an electrolysis cell **1**, a cathode space **2**, and an anode space **3**. In the anode space **3** there is a cation-selective membrane **4**, onto which has been directly mounted an anode **5**. The cation-selective membrane **4** is cation-selective especially by virtue of the immobilizing of negative charges, in this example by means of deprotonated sulfonic acid groups, meaning that predominantly cations can pass through the membrane. In the cathode space **2** is the anion-selective polymer **7**, onto which has been directly mounted the cathode **6**. It is a feature of the anion-selective polymer that it has been modified with quaternary amines NR_4^+, such that predominantly negatively charged ions can pass through this layer.

[0036] In the electrolysis cell **1**, there is pure water as electrolyte. Carbon dioxide is decomposed at the cathode **6**, and hydroxide ions OH^- form together with water. The hydroxide ions OH^- can penetrate the anion-selective polymer, typically in the form of layer **7**. The FIGURE shows the concentration profile of hydroxide ions OH^- and protons H^+ in the cell. The water is decomposed at the anode **5** to give protons and oxygen. The oxygen can leave the electrolysis cell **1** via the anode space **3**. The protons H^+ can cross the cation-selective membrane **4**. This is also shown by the concentration profile of the protons H. At the boundary of the anion-selective polymer layer **7** and the cation-selective membrane **4**, there is now contact between the hydrogen protons H+ and the negatively charged hydroxide ions OH^-. As well as the hydroxide ions OH^-, also present in this region are hydrogencarbonate or carbonate ions (not shown in the concentration profiles), which have formed from unconverted carbon dioxide and hydroxide ions in the cathode space **2**. These can likewise cross the anion-selective polymer layer **7** and come into contact with the hydrogen protons H^+. The hydrogencarbonate or carbonate now reacts with the hydrogen protons H^+ to give water and carbon dioxide. Owing to the porous structure of the anion-selective polymer layer **7**, the carbon dioxide can diffuse back into the cathode space **2**, where it can be reused as reactant. In some embodiments, this increases the yield of the electrolysis cell **1**.

[0037] The efficiency of this electrolysis cell **1** is much higher than in the case of comparable electrolysis cells having a gap. In electrolysis cells having a gap, the cathode has to be divided from the cation-selective membrane in order to avoid unwanted hydrogen production. The anion-selective polymer layer **7** now advantageously enables omission of this gap. In some embodiments, this increases the efficiency of the electrolysis cell since the conductivity of the electrolysis cell is distinctly increased. This likewise enables the use of pure water. In some embodiments, the use of pure water reduces the risk of precipitation of salts or carbonates. This precipitation shortens the lifetime of the electrolysis cell. Thus, the use of pure water prolongs the lifetime of the electrolysis cell.

[0038] In example shown in the FIGURE, the cathode **6** comprises a gas diffusion electrode comprising silver. This enables the preparation of carbon monoxide. This is especially of interest when synthesis gas is to be produced. The use of pure water enables high faraday efficiencies, such that target products can be produced with maximum purity at low voltage.

What is claimed is:

1. An electrolyzer for electrochemical utilization of carbon dioxide, the electrolyzer comprising:
- an electrolysis cell defining
- an anode space and a cathode space;
- an anode in the anode space;
- a cathode in the cathode space;
- a first cation-permeable membrane disposed between the anode space and the cathode space;
- wherein the anode directly adjoins the first cation-permeable membrane; and
- a layer comprising an anion-selective polymer disposed between the first cation-permeable membrane and the cathode;
- wherein the layer covers at least part of the cathode but not all of the cathode.

2. The electrolyzer as claimed in claim **1**, wherein the layer covers a surface area of the first membrane within a range from 20% to 85%.

3. The electrolyzer as claimed in claim **1**, wherein the cathode comprises at least one element selected from the group consisting of: silver, copper, lead, indium, tin, and zinc.

4. The electrolyzer as claimed in claim **1**, wherein the cathode comprises a gas diffusion electrode.

5. A method of operating an electrolyzer for electrochemical utilization of carbon dioxide, the method comprising:
- decomposing carbon dioxide at a cathode disposed in a cathode space of an electrolysis cell;
- forming at least one of carbonate and hydrogencarbonate from unconverted carbon dioxide and hydroxide ions at the cathode;
- transporting hydrogen ions from an anode disposed in an anode space of the electrolysis cell through a first cation-permeable membrane disposed between the anode space and the cathode space;

wherein the anode directly adjoins the first cation-permeable membrane and a layer comprising an anion-selective polymer is disposed between the first cation-permeable membrane and the cathode;

reacting the hydrogen ions and the at least one of carbonate or hydrogencarbonate to produce carbon dioxide and water in a contact region of the layer and the first cation-permeable membrane; and

releasing the carbon dioxide through flow channels and/or pores in the layer.

6. The method as claimed in claim **5**, wherein the electrolyzer is operated with pure water.

7. The method as claimed in claim **5**, further comprising producing at least one of carbon monoxide, ethylene, or formic acid.

8. (canceled)

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