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(54) Benævnelse: **Elektrolysesystem til elektrokemisk kuldioxid-anvendelse med protonafgivelsesenhed og reduktionsfremgangsmåde**

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Description

The present invention relates to a reduction method and to an electrolysis system for electrochemical carbon dioxide utilization. Carbon dioxide is introduced into an electrolysis cell and reduced at a cathode.

State of the art

At present, about 80% of the global energy requirement is covered by the combustion of fossil fuels, the combustion processes of which cause global emission of about 34 000 million tonnes of carbon dioxide into the atmosphere per annum. This release into the atmosphere disposes of the majority of carbon dioxide, which can be up to 50 000 tonnes per day in the case of a brown coal power plant, for example. Carbon dioxide is one of the gases known as greenhouse gases, the adverse effects of which on the atmosphere and the climate are a matter of discussion. Since carbon dioxide is at a very low thermodynamic level, it can be reduced to reutilizable products only with difficulty, which has left the actual reutilization of carbon dioxide in the realm of theory or in the academic field to date.

Natural carbon dioxide degradation proceeds, for example, via photosynthesis. This involves conversion of carbon dioxide to carbohydrates in a process subdivided into many component steps over time and, at the molecular level, in terms of space. As such, this process cannot easily be adapted to the industrial scale. No copy of the natural photosynthesis process with photocatalysis on the industrial scale to date has had adequate efficiency.

An alternative is the electrochemical reduction of carbon dioxide. Systematic studies of the electrochemical reduction of carbon dioxide are still a relatively new field of development. Only in the last few years have there been efforts to develop an electrochemical system that can reduce an acceptable amount of carbon dioxide. Research on the laboratory scale has shown that electrolysis of carbon dioxide is preferably accomplished using metals as catalysts. The publication "Electrochemical CO_2 reduction on metal electrodes" by Y. Hori, published in: C. Vayenas, et al. (eds.), Modern Aspects of Electrochemistry, Springer, New York, 2008, p. 89-189, discloses Faraday efficiencies at different metal cathodes; see table 1. While carbon dioxide is reduced almost exclusively to carbon monoxide at silver, gold, zinc, palladium and gallium cathodes, for example, a multitude of hydrocarbons form as reaction products at a copper cathode.

For example, at a silver cathode, predominantly carbon monoxide and a little hydrogen would form. Possible reactions at anode and cathode can be represented by the following reaction equations:

Cathode: $2\ CO_2 + 4\ e^- + 2\ H_2O \rightarrow 2\ CO + 4\ OH^-$

$2\ CO_2 + 12\ e^- + 8\ H_2O \rightarrow C_2H_4 + 4\ OH^-$

$CO_2 + 8\ e^- + 6\ H_2O \rightarrow CH_4 + 8\ OH^-$

Anode: $2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$

Or alternatively, if a chloride-containing electrolyte is present: $2\ Cl^- \rightarrow Cl_2 + 2\ e^-$

Of particular economic interest, for example, is the electrochemical production of carbon monoxide, methane or ethene. These are higher-energy products than carbon dioxide.

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

Table 1:
The table gives Faraday efficiencies [%] of products that form in the carbon dioxide reduction at various metal electrodes. The values reported apply to a 0.1 M potassium hydrogencarbonate solution as electrolyte and current densities below 10 mA/cm^2.

In the electrochemical conversion of matter of carbon dioxide to a higher-energy product, the increase in the current density and hence the increase in the conversion of matter is of interest. It is not easy to assure a high current density or to increase it even further, since, in the methods known to date and the electrolysis systems used, it is necessary to take account of macrokinetic effects, for instance mass transfer limitations in the immediate proximity of the solid-liquid interface from the electrolyte to the electrode. The carbon dioxide is reduced at the catalytically active cathode surface.

To date, the problem of mass transfer limitation has been countered by the use of gas diffusion electrodes, which can have a process-intensifying effect and have indeed already made existing electrochemical methods economically viable and competitive. Beyond this approach, no further increase in conversion of matter has been possible to date.

Electrolysis cells suitable for electrochemical reduction of carbon dioxide typically consist of an anode space and a cathode space. Figures 2 to 4 show examples of cell arrangements in a schematic diagram. The construction with a gas diffusion electrode is shown, for example, in figure 3. In this execution of an electrolysis cell, the carbon dioxide is introduced through a porous cathode directly from the cathode surface into the cathode space.

US 2013/105304 A1, US 2013/186771 A1, US 2014/093799 A1, US 2012/318680 A1, WO 2013/178803 A1 and WO 2012/128148 A1 disclose electrolysis cells for the reduction of carbon dioxide.

The existing methods of carbon dioxide reduction make use merely of the conversion of carbon dioxide in physically dissolved or gaseous form in the reaction space. None of the known approaches to a solution for carbon dioxide reduction makes use of the chemically bound carbon dioxide content in the electrolysis system: the total molar amount of carbon dioxide present in the electrolysis system is composed of a chemical component and a physical component. Whether the carbon dioxide is in chemically bound or physically dissolved form in the electrolyte depends on various factors, for example the pH, the temperature, the electrolyte concentration or the partial pressure of the carbon dioxide. Both carbon dioxide components are involved in an equilibrium relationship. In the system of carbon dioxide in aqueous carbonate or hydrogencarbonate solution, this equilibrium relationship can be described by the following chemical equation:

$$CO_2+H_2O \rightleftarrows H_2CO_3 \rightleftarrows HCO_3^{-}+H^{+} \rightleftarrows CO_3^{2-}+H^{+} \qquad \text{Eq. 1}$$

As carbonic acid (H_2CO_3) or as carbonate (CO_3^{2-}), for example as potassium carbonate or potassium hydrogencarbonate, as occurs in a system for potash scrubbing, the carbon dioxide is in chemically bound form. But carbon dioxide can also be in gaseous or physically dissolved form. The physical dissolution process also proceeds until establishment of a dissolution equilibrium which, under the assumption of Henry's law, is likewise temperature-, concentration- and pressure-dependent:

$$\chi_i \cdot H_{ij} = P \qquad \text{Eq. 2}$$

In this equation, χ_i represents the molar amount and is less than 0.01. P represents the pressure and is less than 2 bar. H_{ij} represents the Henry constant.

It has been shown, for example in the publication "CO2-reduction, catalyzed by metal electrodes" by Y. Hori, published in: Handbook of Fuel Cells - Fundamentals, Technology and Applications, W. Vielstich et al. (eds.), John Wiley & Sons, Ltd., 2010, p. 2 and fig. 1, that exclusively physically dissolved carbon dioxide is amenable to an electrochemical conversion. If one wished to increase this physically dissolved carbon dioxide according to Henry's law, for example via an elevated partial carbon dioxide pressure P, the result of this would be, according to the chemical equilibrium reaction eq. 1, that a high proportion reacts to give carbonates or hydrogencarbonates and hence the actual carbon dioxide concentration in solution is reduced again.

In spite of the increase in the dissolved carbon dioxide content, with increasing conversion of matter, there is a limitation directly at the electrode surface resulting from the mass transfer from the cathode space to the cathode interface. In such a case, there can also be an increase in unwanted hydrogen production at the reaction surface as a competing process to carbon dioxide reduction. The formation of hydrogen at the cathode surface in turn leads automatically to a very disadvantageous decrease in product selectivity.

Figure 1 shows, by way of illustration of the dependence of the concentration and pH parameters, an example of a Hägg diagram of a 0.05 molar solution of carbon dioxide. Within a moderate pH range, carbon dioxide and salts thereof are present alongside one another. While carbon dioxide (CO_2) is preferentially in the form of carbonate (CO_3^{2-}) in the strongly basic range and preferentially in the form of hydrogencarbonate (HCO_3^-) in the moderate pH range, the hydrogencarbonate ions are driven out of the solution in the form of carbon dioxide at low pH values in the acidic medium. According to the Hägg diagram and equations 1 and 2, the carbon dioxide concentration in a hydrogencarbonate-containing electrolyte can be very low in spite of a high hydrogencarbonate concentration in the range from 0.1 mol/L to well above 1 mol/L up to the solubility limit of the corresponding salt.

It can also be illustrated once again by this diagram that, according to the pH and concentration, a high proportion of carbon dioxide is in chemically bound form and hence is unavailable for the electrochemical utilization.

Consequently, it was found to be necessary for technical purposes to propose an improved solution for electrochemical carbon dioxide utilization which avoids the disadvantages known from the prior art. More particularly, the solution proposed is to enable particularly effective conversion of carbon dioxide. It is an object of the invention to specify an improved production process and electrolysis system for carbon dioxide utilization.

These objects underlying the present invention are achieved by an electrolysis system according to Claim 1 and by a reduction process according to Claim 10. Advantageous configurations of the invention are the subject of the dependent claims.

Description of the invention

The electrolysis system of the invention for carbon dioxide utilization comprises an electrolysis cell having an anode in an anode space, a cathode in a cathode space and at least one membrane, wherein the cathode space has a first feed for carbon dioxide and is configured to bring the carbon dioxide fed in into contact with the cathode. "Membrane" is understood here to mean a mechanically separating layer, for example a diaphragm, which separates at least the electrolysis products formed in the anode space and cathode space from one another. This can also be referred to as a separator membrane or separating layer. Since the electrolysis products can also be gaseous substances, preference is given to using a membrane having a high bubble point of 10 mbar or higher. The "bubble point" is a defining parameter for the membrane used, which describes the pressure difference ΔP between the two sides of the membrane from which gas flow through the membrane would set in.
Carbon dioxide in chemically bound form, for example as carbonate or hydrogencarbonate in the electrolyte, can be introduced into the cathode space via the first feed for carbon dioxide, or else carbon dioxide gas can be introduced into the cathode space via the first feed separately from the electrolyte or physically dissolved carbon dioxide in an electrolyte. More particularly, the feed is the electrolyte and reactant inlet. Even when the carbon dioxide enters the cathode space in gaseous or dissolved form, a proportion thereof enters into a chemical compound with substances present in the electrolyte according to the equilibrium reactions described above, especially when the pH is basic.

The electrolysis system additionally has a proton donor unit and the cathode space is connected to the proton donor unit via a second feed for protons. The second feed for protons is configured such that the protons are brought into contact with the cathode surface in the cathode space. The proton donor unit is defined here in that free protons, i.e. hydrogen cations, are indeed provided. Hydrogen (H_2) or other hydrogen compounds are not protons for the purposes of the proton donor unit of the invention.

By means of the proton donor unit, local lowering of the pH is possible in the electrolysis system, which promotes the formation of physically dissolved carbon dioxide at the reaction interface of the cathode and significantly increases the conversion of matter.

The electrolysis system comprises a proton donor unit having a proton reservoir and a proton-permeable membrane. The proton-permeable membrane functions here as a second feed to the cathode space for the protons. While the proton reservoir offers the advantage of continuous replenishment of protons, the proton-permeable membrane serves to assure pure ion flow or proton flow to the cathode space and simultaneously to retain other molecules, liquids or gases. The proton-permeable membrane preferably comprises sulfonated polytetrafluoroethylene. Alternatively, it is possible to use a cation exchange membrane as proton-permeable membrane.

In one embodiment of the invention, the electrolysis system has an acid reservoir as proton reservoir which especially comprises a Brønsted acid. A Brønsted acid is, for example, sulfuric acid, phosphoric acid, nitric acid, hydrochloric acid or else various organic acids, for example acetic acid or formic acid. The definition of an acid according to Brønsted describes acids as so-called proton donors, i.e. particles that can release protons, i.e. positively charged hydrogen ions. According to the definition of the pKa, i.e. according to equation 1, preference is given to using Brønsted acids having a pKa correspondingly smaller than the pKa of aqueous carbonate, hydrogencarbonate or dihydrogen carbonate solution. "Smaller" in this case means that the acid is stronger.

One advantage of the acid reservoir is that it provides a relatively continuous proton source which is not reliant on an additional external energy input.

In a further embodiment of the invention, the electrolysis system has a second proton-permeable membrane comprising sulfonated polytetrafluoroethylene. The proton-permeable membrane used is preferably a Nafion membrane.
This membrane may be executed, for example, in multilayer or porous form. The first membrane used, i.e. the separator membrane, may likewise be a proton-permeable membrane, like that of the proton donor unit.

Typically, the cathode space of the electrolysis system comprises a catholyte/carbon dioxide mixture, wherein the catholyte comprises carbonate and/or hydrogencarbonate anions. In addition, the catholyte in the cathode space of the electrolysis system especially comprises alkali metal and/or ammonium ions (NH_4^+). Alkali metals refer to the chemical elements lithium, sodium, potassium, rubidium, cesium and francium from the first main group of the Periodic Table. The carbonate- and/or hydrogencarbonate-containing electrolyte has the advantage of including chemically bound carbon dioxide. Alternatively or additionally, carbon dioxide can be introduced into the cathode space in dissolved or gaseous form. The pH of the catholyte in the cathode space preferably has a value between 4 and 14.

In a further advantageous embodiment of the invention, the electrolysis system comprises an anode space which functions as proton reservoir. It is possible here, for example, to use an electrolysis system in which a single proton-permeable membrane simultaneously fulfills the function of separating cathode space and anode space and the function of admitting protons into the cathode space. Alternatively, the anode space which functions as the proton reservoir is connected to the cathode space by the membrane and an anode in porous form. Further alternatives will be apparent from the embodiments that are still to follow that have two proton reservoirs, for example including connected proton reservoirs. It is not absolutely necessary for the proton reservoirs to be connected, since protons can also be produced again at the anode, which depends on the electrolyte concentration. The concentration has to be correspondingly high for the release of carbon dioxide.

The electrolysis system has a first membrane and a second membrane, wherein the first membrane is arranged between the anode and cathode as separator membrane, the second membrane is arranged between the cathode and proton reservoir, and at least this second membrane is proton-permeable. This arrangement of the electrolysis system is advantageous since the connection of the proton reservoir via the proton-permeable membrane to the cathode ensures that the protons are supplied directly to the reaction surface of the cathode. For this purpose, the cathode is preferably in porous form and is in direct, two-dimensional contact with the proton-permeable membrane adjoining the proton reservoir. In this setup, for example, anolyte, catholyte and proton source, for example an acid or acid mixture, can be chosen separately from one another and preferably matched to one another.

In a further advantageous embodiment of the invention, the cathode space of the electrolysis system is in the form of a catholyte gap that extends along the cathode and has a width, i.e. an extent at right angles to the surface area of the cathode, of not more than 5 mm. A catholyte gap is accordingly understood to mean a thin hollow space in two-dimensional form between the cathode and a membrane. The membrane bounds the catholyte gap, for example, from the proton reservoir or from the anode space or the anode. In the case of a greater gap width than 5 mm, the pH gradient described again plays a non-negligible role in the cathode space.

Preferably, the cathode space in the electrolysis system is executed as a catholyte gap which separates the cathode and proton-permeable membrane or the cathode and the first membrane, and these are each arranged at a distance of not more than 5 mm from one another.

In further-developed embodiments of the electrolysis system described, the cathode space may also comprise two catholyte gaps arranged on either side of the cathode, each of which is bounded by a membrane, wherein the cathode and membranes are each independently arranged at a maximum distance of 5 mm from one another. In this way, electrolysis products can be generated on both sides of the cathode. These embodiments have the benefit that it is possible to use a solid cathode, i.e., for example, a cathode sheet, meaning that the cathode is not in porous form. A solid cathode of this kind preferably has a nanostructured surface. In the case of the embodiment with a solid cathode, both membranes are in proton-permeable form in order to correspondingly assure proton access.

Particularly suitable embodiments of the invention are accordingly characterized by a small distance between proton-conducting membrane and cathode, or between separator membrane and cathode in the case of the integrated proton donor cathode: this distance is typically between 0 and 5 mm, preferably between 0.1 and 2 mm. A distance of 0 mm would correspond to a polymer electrolyte membrane (half-)cell.

In an alternative embodiment of the invention, the electrolysis system comprises a proton donor cathode comprising the proton donor unit and a proton-permeable cathode integrated therein. In this case, the cathode is porous, i.e., for example, in the form of a perforated sheet electrode, of a sieve electrode, of a lattice electrode, mesh electrode or weave electrode or, like a gas diffusion electrode, composed of compressed nano- to microparticles, optionally with additional membrane plies. The proton-permeable cathode here is preferably bonded directly to, for example applied to, the proton-permeable membrane, or vice versa, and hence forms part of the second feed to the cathode space for the protons. In this configuration, the protons enter the cathode space from the proton reservoir over the entire cathode area, i.e. exactly at the point in the cathode space, and the phase interface between cathode surface and catholyte, at which they are to release the carbon dioxide from the catholyte. According to their function and arrangement, this variant was referred to as proton donor cathode.

Firstly, the proton-donating membrane of the proton donor unit can thus be arranged in the immediate proximity of the cathode; secondly, the cathode can be integrated into the proton donor unit with the proton-donating membrane.

In the reduction method of the invention for carbon dioxide utilization by means of an electrolysis system according to any of the embodiments described, a catholyte/carbon dioxide mixture is introduced into a cathode space and brought into contact with a cathode, and local lowering of the pH of the catholyte/carbon dioxide mixture is undertaken in the cathode space by providing additional protons. The additional protons in that case serve to produce reducible carbon dioxide which is in physically dissolved or gaseous form but is no longer chemically bound, this carbon dioxide being generated or released directly at the cathode reaction interface. This local increase in carbon dioxide concentration significantly increases the conversion thereof.

In a preferred embodiment of the invention, in the reduction method, the local lowering of the pH of the catholyte/carbon dioxide mixture is undertaken at the liquid/solid phase interface from the catholyte/carbon dioxide mixture to the cathode by providing the additional protons via the proton-permeable membrane or via the proton-permeable cathode at the liquid/solid phase interface from the catholyte/carbon dioxide mixture to the cathode. This brings about in situ carbon dioxide generation in the phase interface region from the hydrogencarbonate or carbonate anions present in the electrolyte.

In a further preferred embodiment of the invention, in the reduction method, protons are taken from a proton reservoir, especially an acid reservoir which especially comprises a Brønsted acid, e.g. sulfuric acid, phosphoric acid or nitric acid, hydrochloric acid or an organic acid such as acetic acid and formic acid.

In a further advantageous variant of the reduction method, the catholyte includes carbonate and/or hydrogencarbonate anions and/or dihydrogen carbonate. In addition, the catholyte preferably includes alkali metal and/or ammonium ions. Alternatively or additionally, the catholyte includes sulfate and/or hydrogensulfate ions, phosphate, hydrogenphosphate and/or dihydrogenphosphate ions.

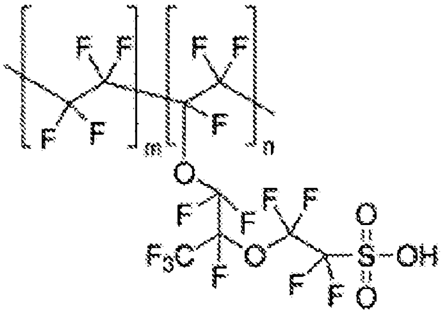
Preferably, the pH of the catholyte is within a range between 4 and 14.

In the working example, by virtue of a conductive porous catalyst cathode being integrated into the proton donor unit in such a way that the protons are introduced into the cathode space via the proton-conducting membrane and directly thereafter through the cathode itself, the proton-conducting membrane can be backflushed, for example, by an acid. The acid strength here is preferably adjusted such that the amount of carbon dioxide driven out of the catholyte is specifically as much as can be reduced at the cathode at a given current density. This has the particular advantage that it is possible in this way to ensure that the product formed or the product mixture is very low in carbon dioxide.

The cathode itself preferably has a high surface area. In the case of a polymer electrolyte membrane (PEM) setup, the cathode itself is preferably in porous form, which likewise means an increase or maximization in the reactive surface area. The cathode used is preferably an RVC (reticulated vitreous carbon) electrode. This has the advantage of also being permeable to the electrolyte itself and, by contrast to a gas diffusion electrode, having no hydrophobic constituents. This would likewise be an example of a preferred embodiment of the invention with use of an electrolysis cell as shown in figure 4. In a further preferred embodiment, the cathode used is a silver gas diffusion electrode. What is important here is that this can also be executed with zero carbon content. A silver gas diffusion electrode used comprises, for example, silver (Ag), silver oxide (Ag_2O) and polytetrafluoroethylene (PTFE, e.g. Teflon).

The invention described thus enables the conversion of the carbon dioxide content chemically bound in carbonates and hydrogencarbonates to physically dissolved carbon dioxide or carbon dioxide gas, which constitutes the desired starting components for the electrochemical carbon dioxide reduction. What are thus described are a method and a system that enable high carbon dioxide conversions with current densities $>> 100$ mA/cm^2, without requiring an electrode with separate gas supply as cathode. A gas diffusion electrode as used to date could be introduced as an additional component in one embodiment of the invention. The phase interface layer between the proton-conducting membrane of the proton donor unit and the catholyte or the phase interface layer between the cathode surface and the catholyte effectively itself serves as a carbon dioxide source. In this phase interface layer, a local change in pH occurs as a result of the migrating protons. The equilibrium reaction 1 is then affected in such a way that finely divided carbon dioxide gas bubbles arise at the membrane surface or cathode surface through breakdown of carbonate in the acidic medium. According to the embodiment, the locally acidic pH is also determined by the Brønsted-acidic surface of the proton-conducting membrane or by the acidic sulfonic acid groups that exist at the cathode surface. The sulfonic acid groups come from the sulfonated polytetrafluoroethylene in the membrane. The latter comprises, for example, Nafion, i.e. Teflon additionally containing a directly coupled sulfonic acid group. In water, this polymer swells to give a kind of "solid" sulfuric acid. The cations are then conducted from sulfonic acid group to sulfonic acid group in a kind of hopping transport. Protons can be conducted by tunnelling or hopping particularly efficiently through the Nafion. Divalent cations are more likely to get stuck and not be transported any further. Reference is therefore also made to polymer ion exchangers.

An example of a structural formula of sulfonated polytetrafluoroethylene:



The cause of the formation of gaseous carbon dioxide is attributable to neutralization of the hydronium ions that pass through by means of carbonate or hydrogencarbonate ions that are present. A strongly acidic electrolyte, for example a strongly acidic anolyte, can additionally enhance this effect: in the example that the anode space serves as a proton reservoir, an elevated proton pressure on the membrane is generated from the anode side and amplifies the concentration gradient in the cathode space. In this example, the anolyte, as described, may comprise a Brønsted acid, for example sulfuric acid, phosphoric acid or nitric acid.

In the catholyte, preference is given to using alkali metal or ammonium ions or hydrogencarbonates or carbonates. In the course of the carbon dioxide reduction, the starting composition of the catholyte, especially the hydrogencarbonate or carbonate concentration thereof, can be restored via the introduction or dissolution of carbon dioxide. An operation of this kind can be implemented, for example, as described, by the additional use of a gas diffusion electrode.

What has thus been presented is a proton-donating cathode in an arrangement for carbon dioxide reduction, which enables conversion of the hydrogencarbonate and carbonate ions present in the electrolyte to carbon dioxide. By the method presented, it is possible to get round the limitation of solubility of gaseous carbon dioxide in the immediate proximity of the reactive sites. Since only neutral carbon dioxide is electrochemically reducible, and carbonate and hydrogencarbonate that are the chemical equilibrium species thereof are not, this is a very advantageous approach for increasing the conversion of matter and hence also for achieving high current densities. In addition, it is thus possible to avoid or additionally assist pressurization of the system as has been undertaken to date, for example, for increasing the carbon dioxide saturation.

The process-intensifying method that has been presented for the electrochemical reduction of carbon dioxide improves the conversion of matter per unit electrode area and per unit current density. At the same time, undesirably high carbonate and hydrogencarbonate concentrations in the electrolyte, especially in the catholyte, are avoided, these having an adverse effect on the physical solubility of the carbon dioxide. The principle of a gas diffusion electrode established in industry can be replaced by the method described. The gas diffusion electrode can, however, further be used as an add-on to this new principle described, for example for the replenishment of carbon dioxide in the electrolyte circuit. The method is particularly suitable for use in electrolysis cells with external carbon dioxide saturation.

A particularly suitable application of the process described lies in the workup of the potassium hydrogencarbonate solution obtained in basic carbon dioxide potash scrubbing within the scope of an in situ electrochemical regeneration of the laden absorbent. Compared to conventional thermal regeneration, the method offers enormous energy-saving potential.

Examples and embodiments of the present invention are still to be described by way of example with reference to figures 1 to 9 of the appended drawings:

figure 1	shows a Hägg diagram for a 0.05 molar carbon dioxide solution,
figure 2	shows a schematic diagram of a two-chamber setup of an electrolysis cell,
figure 3	shows a schematic diagram of a three-chamber setup of an electrolysis cell,
figure 4	shows a schematic diagram of a PEM setup of an electrolysis cell,
figure 5	shows an electrolysis cell in a two-chamber setup and the characteristic rise in pH toward the cathode,
figure 6	shows a schematic diagram of a cell arrangement with an additional acid reservoir and porous cathode,

figure 7 shows a cell arrangement with an additional acid reservoir and two catholyte gaps,

figure 8 shows a schematic diagram of a further example of a cell arrangement with an additional acid reservoir and porous cathode and

figure 9 shows a schematic diagram of a further embodiment of a cell arrangement with an additional acid reservoir and electrolyte gaps.

The Hägg diagram shown in figure 1 contains values for a 0.05 molar solution of carbon dioxide in water: the concentration of C in the unit mol/L is plotted against the pH. The proton concentration (H^+), starting from a pH > 0, drops from 1 to a value of 10^{-10} mol/L at a pH of 10, while the OH^- ion concentration rises in accordance with the definition of pH. Thus, while there is still a virtually pH-independent carbon dioxide concentration (CO_2) of 0.05 mol/L in an acidic medium, i.e. up to a pH of about 4, this drops significantly starting from a pH of 5, in favor of a rise in the hydrogencarbonate ions (HCO_3^-), which have their highest concentration within a pH range between 8 and 9. In a basic medium at very high pH values > 12, carbon dioxide is predominantly in the form of carbonate ions (CO_3^{2-}) in the solution.

The standard setups of electrolysis cells 2, 3, 4 shown in schematic form in figures 2 to 4 comprise at least one anode A in an anode space AR and a cathode K in a cathode space KR. In each of the cases, the anode space AR and cathode space KR are separated from one another at least by a membrane M_1. This membrane M1 preferably ensures the separation of the gaseous products G1 and products P1, or prevents mixing. A defining parameter for the membrane M1 is what is called the bubble point. This describes the pressure difference ΔP between the two sides of the membrane M1 from which gas flow would take place through the membrane M1. Thus, preference is given to using a membrane M1 having a high bubble point of 10 mbar or higher. The membrane M_1 here may be an ion-conducting membrane, for example an anion-conducting membrane or a cation-conducting membrane. The membrane may be a porous layer or a diaphragm. Lastly, the membrane M1 may also be understood to mean an ion-conducting spatial separator that separates electrolytes into anode space and cathode space AR, KR. According to the electrolyte solution E used, a setup without a membrane M_1 would also be conceivable. Anode A and cathode K are each connected electrically to a voltage supply. The anode space AR of each of the electrolysis cells 2, 3, 4 shown is equipped with an electrolyte inlet 21, 31, 41. Likewise, each anode space AR depicted comprises an electrolyte outlet 23, 33, 43, via which the electrolyte E and electrolysis products G1 formed at the anode A, for example oxygen gas O_2, can flow out of the anode space AR. The respective cathode spaces KR each have at least one electrolyte outlet and product outlet 24, 34, 44. The overall electrolysis product P1 here may be composed of a multitude of electrolysis products.

While anode A and cathode K in the two-chamber setup 2 are in an arrangement separated from the membrane M_1 by the anode space AR and cathode space KR, the electrodes in what is called a polymer electrolyte membrane (PEM) setup 4 with porous electrodes directly adjoin the membrane M_1. As shown in figure 4, the anode is then a porous anode A and the cathode is a porous cathode K. In the two-chamber setup 2 and in the PET setup 4, the electrolyte and the carbon dioxide CO_2 are preferably introduced into the cathode space KR via a common reactant inlet 22, 42.

In a different manner, as shown in figure 3, in what is called a three-chamber setup 3, in which the cathode space KR has an electrolyte inlet 32, the carbon dioxide CO_2 is fed into the cathode space KR separately therefrom via the cathode K, which in this case is necessarily in porous form. Preferably, the porous cathode K is configured as a gas diffusion electrode

GDE. A gas diffusion electrode GDE is characterized in that the liquid component, for example an electrolyte, and a gaseous component, for example an electrolysis product, can be contacted with one another in a pore system of the electrode, for example the cathode K. The pore system of the electrode is in such a form that the liquid and gaseous phase alike can penetrate into the pore system and be present simultaneously therein. Typically, for this purpose, a reaction catalyst is in porous form and assumes the electrode function, or a porous electrode includes catalytically active components. For introduction of the carbon dioxide CO_2 into the catholyte circuit, the gas diffusion electrode GDE comprises a carbon dioxide inlet 320.

It would be possible to implement the invention, for example, in one of the electrolysis cell setups known to date, as shown, for example, in figures 2 and 3, if they were to be provided with an appropriate proton donor unit. The setup shown in figure 4 would require more specific modifications for the implementation of the invention, for example transport channels for the electrolyte through the cathode, in order to establish membrane-electrolyte contact. Preferably, in these transport channels, carbon dioxide evolution or release would take place. Analogously, on the anode side, transport channels for the analyte to the membrane are required in order thus to provide the protons. By means of a polymer electrolyte setup of this kind with porous electrodes having transport channels, it is possible to implement a very advantageous case in which almost exactly as much carbon dioxide is produced as is then also reduced at the cathode. In this way, by contrast with the gas diffusion electrode, as described in the prior art to date, it is possible to arrive at particularly highly enriched products. The electrolysis cells known from the prior art can also be modified for the use according to the invention in such a way that they are combined to give mixed variants. For example, an anode space may be executed as a polymer electrolyte membrane half-cell, whereas a cathode space consists of a half-cell, with cathode space between membrane and cathode, as shown in figures 2 and 3.

Figure 5 shows, in schematic form, the setup of an electrolysis cell 5 with an anode space AR between an anode A and a membrane M1, and a cathode space KR between the membrane M1 and the cathode K. Anode A and cathode K are connected to one another via a voltage supply. An arrow from the anode space AR into the cathode space KR through the membrane M1 indicates that it is ion-conducting at least to one type of charge carrier, preferably at least to cations X^+, where these can be different metal cations X^+ depending on which anolyte is used, and to protons H^+. The cathode space KR has a width d_{MK}, i.e. a distance between membrane M1 and cathode K. The membrane M1 and the cathode K are arranged in the electrolysis cell 5 such that the surfaces thereof facing the cathode space KR run plane-parallel to one another. A slope triangle indicates the pH gradient in the cathode space KR: the pH rises from a locally acidic environment close to the membrane M1 to a locally basic environment close to the cathode surface K. The locally acidic region is identified by I and represented by a dotted line parallel to M1; correspondingly, II and the dotted line in front of the cathode K show the region which is locally basic in the cathode space KR. The anode space AR becomes acidic to the same degree as the cathode space KR becomes basic.

Another look at the equilibrium reaction 1 explains the pH gradient as follows: the anions and cations that are present and form on the different sides of the membrane M1 can migrate, within the electrolyte E and through the membrane M1. The electrons provided at the anode A, for example in an aqueous electrolyte E, convert the water to H^+ ions and oxygen gas O_2. If carbon dioxide CO_2 is, for example, in chemically bound form as hydrogencarbonate HCO_3^- in the anolyte and/or catholyte, it can react further with the protons H^+ to give carbon dioxide gas CO_2 and water H_2O. The catholyte preferably comprises alkali metal and/or ammonium ions or the hydrogencarbonates or carbonates thereof. The reaction of hydrogencarbonate HCO_3^- to give carbon dioxide CO_2 is referred to as the acidic breakdown of hydrogencarbonate HCO_3^-. In a basic medium, i.e. at a pH between 6 and 9, hydrogencarbonate HCO_3^- is formed, meaning that the equilibrium reaction eq. 1 then runs the other way. Thus, if a potassium hydrogencarbonate solution, for example, is then used as anolyte and as catholyte in an electrolysis cell 5, the pH gradient shown in figure 5 from a locally acidic environment I forms in the phase boundary layer between M1 and catholyte, in which the carbon dioxide is preferentially released. At the cathode surface or in the phase boundary layer II between the cathode surface and catholyte, however, the pH, owing to ion migration, is already sufficiently high again, for example within a range between 6 and 9, that the reaction of potassium hydrogencarbonate formation predominates and hence only little physically bound carbon dioxide CO_2 is available in the electrolyte solution E for reduction at the cathode K.

The distance d_{MK} accordingly has to be chosen at such a minimum level that the phase interface layer I between the membrane M1 and catholyte that functions as the carbon dioxide source abuts, or overlaps or coincides with, the phase interface layer II between the cathode surface K and catholyte, such that sufficient released carbon dioxide CO_2 is provided or replenished at the reaction interface of the cathode K.

Figures 6 to 9 show preferred embodiments of electrolysis cells according to the invention. These are in principle designed according to the polymer electrolyte membrane (PEM) setup, or polymer electrolyte membrane half-cell setup. Firstly, the proton-donating membrane of the proton donor unit can be arranged in the immediate proximity of the cathode, as in figures 7 and 9; secondly, the cathode can be integrated into the proton donor unit with the proton-donating membrane, as shown by way of example by figures 6 and 8.

The polymer electrolyte membrane (PEM) is frequently also called proton exchange membrane and is a semipermeable membrane. These membranes are preferably permeable to cations such as protons H^+, lithium cations Li^+, sodium cations Na^+ or potassium cations K^+, while the transport of gases, for example oxygen O_2 or hydrogen H_2, is prevented. This purpose is fulfilled by the membrane M_1, for example in the separation of the products P1, G1 of the anode and cathode reactions. In most cases, aqueous liquids can flow through the PEM, although the capillary forces inhibit this transport. A polymer electrolyte membrane may be produced, for example, from an ionomer, pure polymer membranes or composite membranes, wherein other materials are embedded into a polymer matrix. One example of a commercially available polymer electrolyte membrane is Nafion from DuPont.

All setups have the same sequence of, on the left-hand side, an anode space AR separated from the cathode space KR by an anode A and a membrane M1 abutting the side of the anode A facing away from the anode space AR. The cathode space KR is abutted by the cathode K, and the latter by the proton donor unit in different designs. Arrows indicate the reactant and electrolyte inlets E into the anode space AR and cathode space KR, and the outlets for electrolyte mixtures E and product mixtures P1, G1. The membrane M1 serves predominantly as separator membrane, but may also be proton-permeable, as required, for example, for the embodiment with an additional acid reservoir PR1 on the anode side. The acid or proton reservoir PR on the cathode side is divided from the cathode K in all cases by a proton-conducting membrane M2. In figures 7 and 9, the cathode K is between two catholyte gaps KS or integrated into the proton donor unit as a proton donor cathode PSK. In the cases of the cell arrangement as shown in figures 6 and 8, the porous cathode K is not just in proton-permeable form, but preferably also electrolyte-permeable form, such that the carbon dioxide release can occur over a very large cathode surface area, for example within electrolyte channels, in the cathode K. In the examples with solid cathode K and a very narrow cathode space, which should instead be referred to as catholyte gap KS, owing to its small extent between the reactive area and the membrane surface M2, via which the protons H^+ are preferably supplied, the cathode K may be formed from a solid metal sheet, but may also have advantageous nanostructuring to increase the surface area. In the case of division of the cathode space KR into two catholyte gaps KS, as shown in figures 7 and 9, the acid flowing past the cathode K can form the anolyte, since protons H^+ are then generated on the anode side by water oxidation, for example. In figures 8 and 9, the anode space AR is explicitly designed as an additional proton reservoir PR1 and the anolyte used is an acid. In these cases, the two proton or acid reservoirs PR, PR1 may be connected to one another via a circulation system (circuit not shown in figures 8 and 9). The catholyte gaps KS shown in figures 7 and 9 have a width, for example, between 0 and 5 mm, advantageously between 0.1 and 1 mm, preferably between 0.1 and 0.5 mm. In the cases shown in figures 8 and 9, the separator membrane M1 may be in proton-conducting form; at least one membrane M1 that ensures charge balance is used.

For the cases shown in figures 6 and 9 with proton donor cathode PSK and cathode space KR, however, it is important not to arbitrarily constrict the cathode space KR and to reduce it to a cathode gap KS: in these cases, a minimum distance b_{KR} is actually necessary between separator membrane M1 and proton donor cathode PSK, since the hydronium ions that pass through, given too small an electrolyte volume between separator membrane M1 and cathode K, would otherwise be converted primarily to hydrogen H_2 at the catalyst interface, and hence no carbon dioxide reduction could take place. The protons H^+ that enter the cathode space KR must firstly ensure the carbon dioxide formation and must not be converted directly to hydrogen H_2. The minimum distance b_{KR} for the cathode space KR in the case of a cell arrangement 6, 8 with proton donor cathode PSK is 1 mm. Preferably, the distance b_{KR} between separator membrane surface M1 and catalyst surface K is between

1 and 10 mm, preferably not more than 5 mm, advantageously not more than 2 mm.

By means of the invention, it is accordingly possible to set the absolute carbon dioxide concentration of the liquid phase, but in particular the local availability of the physically dissolved carbon dioxide in the immediate proximity of the electrode surface. Macrokinetic mass transfer operations play only a minor role in the arrangement of the invention, since the carbon dioxide required for electrochemical reduction is effectively provided from the anions of the electrolyte by in situ protonation at the reaction surface.

Patentkrav

1. Elektrolysesystem til kuldioxid-anvendelse, omfattende en elektrolysecelle (6, 7, 8, 9) med en anode (A) i et anoderum (AR), en katode (K) i et katoderum (KR) og en første og en anden membran (M1, M2), hvor katoderummet (KR) har en første adgang til kuldioxid (CO_2) og er udformet til at bringe det tilførte kuldioxid (CO_2) i kontakt med katoden (K), hvor elektrolysesystemet omfatter en protonafgivelsesenhed, og katoderummet (KR) er forbundet med protonafgivelsesenheden via en anden adgang til protoner (H^+), der er udformet til at bringe protonerne (H^+), der er tilført til katoderummet (KR), i kontakt med katoden (K), hvor protonafgivelsesenheden omfatter et protonreservoir (PR) og en protongennemtrængelig membran (M2), der fungerer som anden tilgang til katoderummet (KR) til protonerne (H^+), hvor den første membran (M1) er anbragt mellem anode (A) og katode (K), den anden membran (M2) er anbragt mellem katode (K) og et protonreservoir (PR), og i det mindste den anden membran (M2) er protongennemtrængelig.

2. Elektrolysesystem ifølge krav 1, hvor protonreservoiret (PR) er et syrereservoir, der især omfatter en Brønstedsyre (HX).

3. Elektrolysesystem ifølge et af de foregående krav 1 eller 2, hvor den protongennemtrængelige membran (M2) omfatter sulfoneret polytetrafluorethylen.

4. Elektrolysesystem ifølge et af de foregående krav, hvor katoderummet (KR) omfatter en katolyt-kuldioxid-blanding, hvor katolytten omfatter carbonat- (CO_3^{2-}) og/eller hydrogencarbonat-anioner (HCO_3^-) og/eller dihydrogencarbonat (H_2CO_3).

5. Elektrolysesystem ifølge et af de foregående krav, hvor anoderummet (AR) fungerer som supplerende protonreservoir (PR1).

6. Elektrolysesystem ifølge et af de foregående krav, hvor katoderummet (KR) er udformet som katolytspalte (KS), der strækker sig langs katoden (K) og har et omfang vinkelret på katodefladeudstrækningen på maksimalt 5 mm.

7. Elektrolysesystem ifølge krav 6, hvor katoderummet (KR) er udformet som katolytspalte (KS), der adskiller katode (K) og membran (M1, M2), hvor katoden (K) og membranen (M1) er anbragt i en afstand på maksimalt 5 mm i forhold til hinanden.

8. Elektrolysesystem ifølge krav 7, hvor katoderummet (KR) omfatter to katolytspalter (KS), der er anbragt på hver side af katoden (K) og hver især er begrænset af en membran (M1, M2), hvor katoder (K) og membraner (M1, M2) hver især uafhængigt af hinanden er anbragt i en afstand på maksimalt 5 mm i forhold til hinanden.

9. Elektrolysesystem ifølge et af de foregående krav 1 til 6 med en protonafgivelseskatode (PSK), der omfatter protonafgivelsesenheden og deri integreret protongennemtrængelig katode (KP), der er porøs.

10. Reduktionsfremgangsmåde til kuldioxid-anvendelse ved hjælp af et elektrolysesystem ifølge et af de foregående krav,
hvor en katolyt-kuldioxid-blanding indføres i et katoderum (KR) af et elektrolysesystem ifølge et af de foregående krav og bringes i kontakt med en katode (K),
og hvor der i katoderummet (KR) foretages en lokal pH-værdi-sænkning af katolyt-kuldioxid-blandingen, idet yderligere protoner (H^+) tilvejebringes.

11. Reduktionsfremgangsmåde ifølge krav 10, hvor den lokale pH-værdi-sænkning af katolyt-kuldioxid-blandingen foretages på fasegrænsefladen mellem flydende og fast af katolyt-kuldioxid-blandingen til katoden (K), idet de yderligere protoner (H^+) tilvejebringes via den protongennemtrængelige membran (M2) eller via en protongennemtrængelig katode (KP) ved fasegrænsefladen mellem flydende og fast af katolyt-kuldioxid-blandingen til katoden.

12. Reduktionsfremgangsmåde ifølge krav 10 eller 11, hvor protonerne (H^+) udtages fra protonreservoiret (PR), især et syrereservoir, der især omfatter en Brønstedsyre (HX), f.eks. svovlsyre (H_2SO_4), phosphorsyre (H_3PO_4) eller salpetersyre (HNO_3), saltsyre (HCl) eller organiske syrer, såsom eddikesyre og myresyre.

13. Reduktionsfremgangsmåde ifølge et af de foregående krav 10 til 12, hvor katolytten omfatter carbonat- (CO_3^{2-}) og/eller hydrogencarbonat-anioner (HCO_3^-).

FIG 1

Prior Art

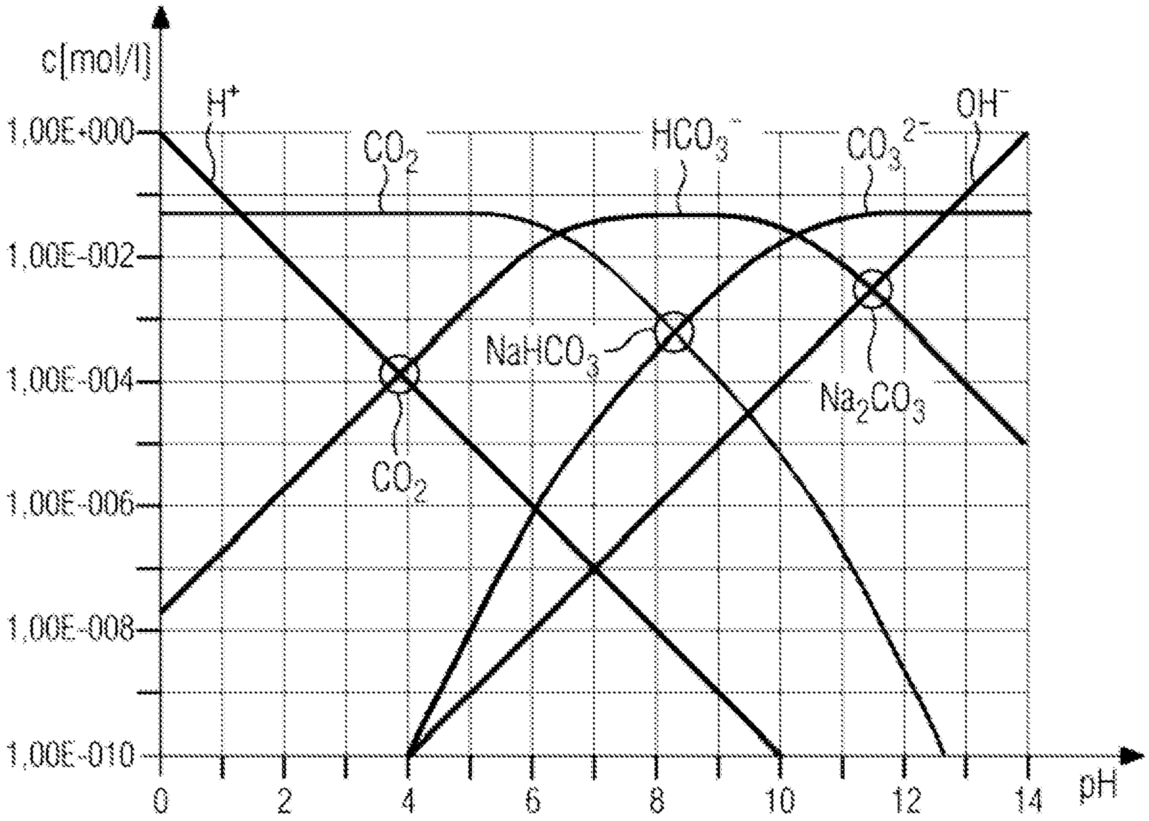


FIG 2

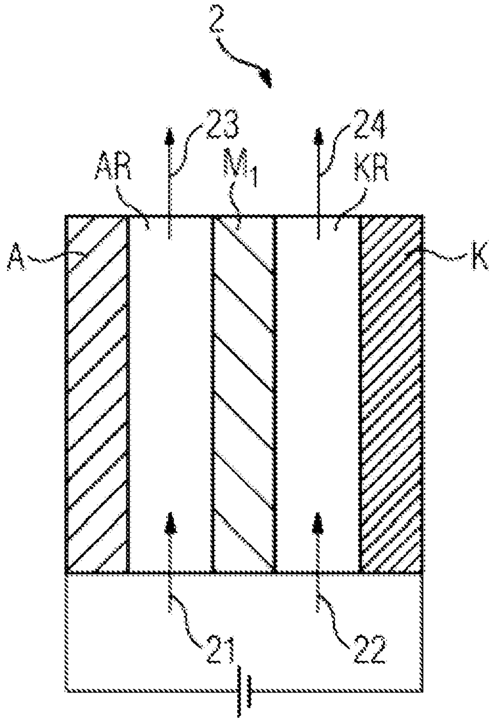


FIG 3

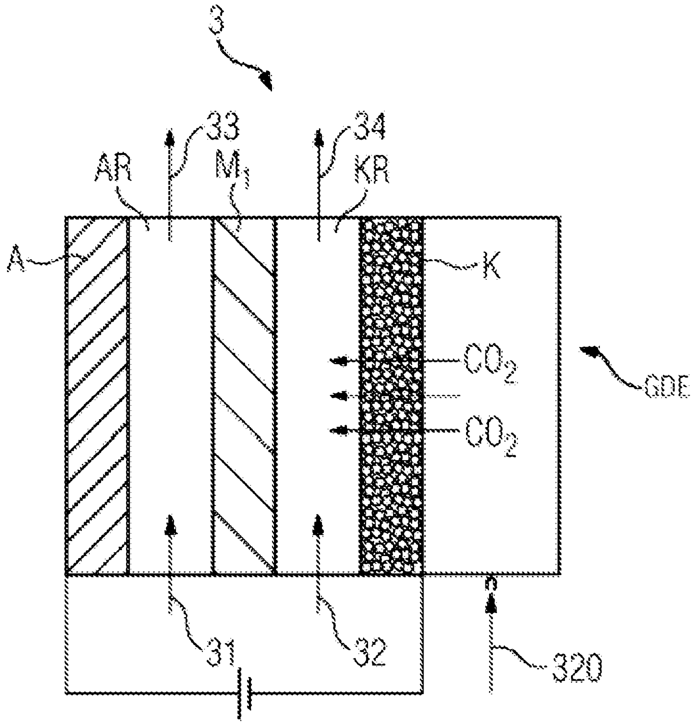


FIG 4

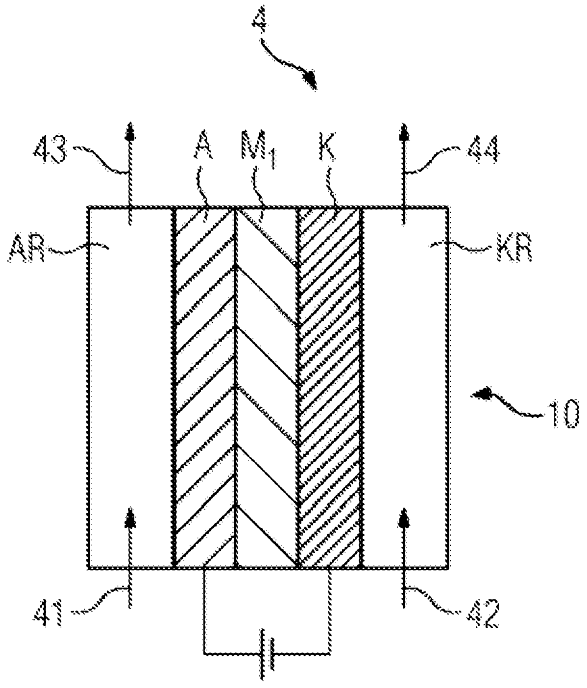


FIG 5

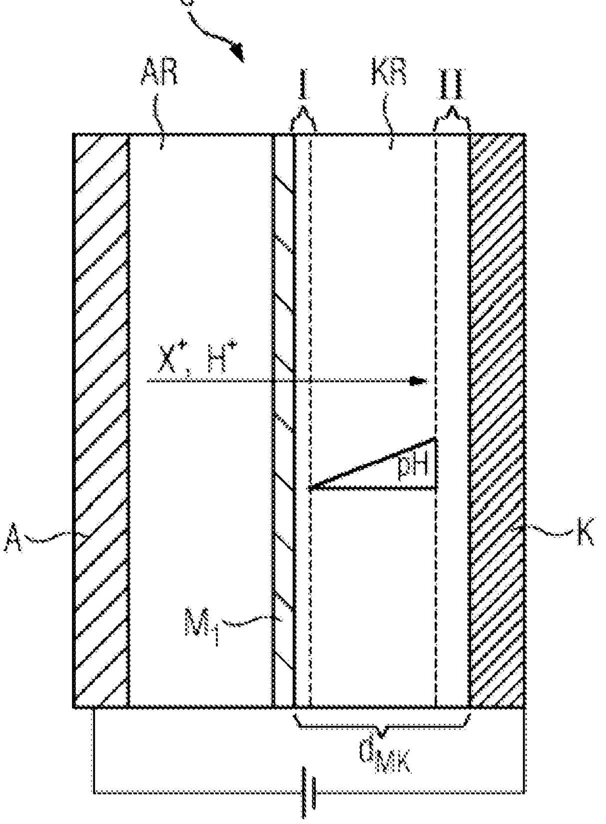


FIG 6

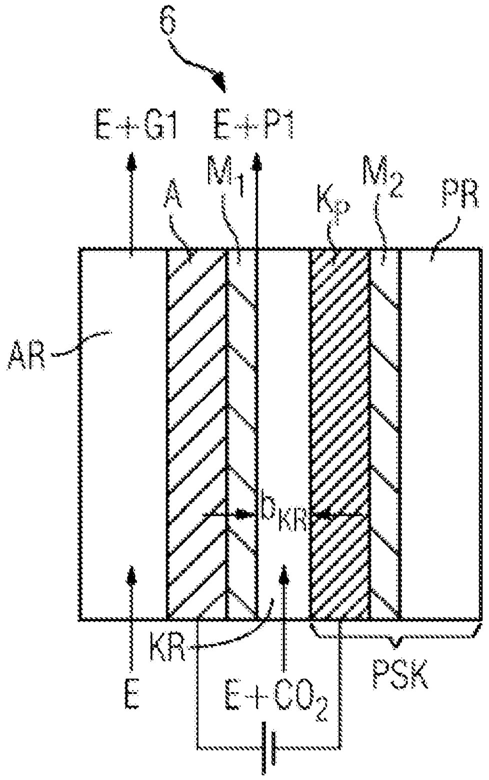

6
E+G1
E+P1
A
M_1
K_P
M_2
PR
AR
D_{KR}
KR
E
E+CO_2
PSK

FIG 7

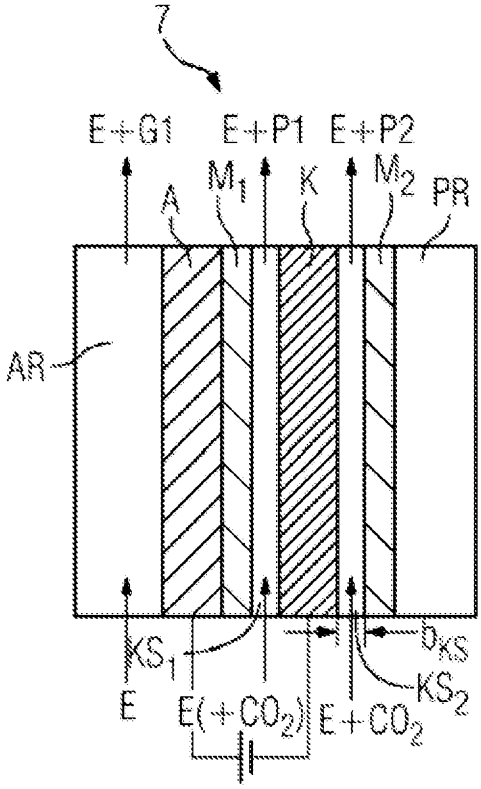

7
E+G1
E+P1
E+P2
A
M_1
K
M_2
PR
AR
KS_1
D_{KS}
KS_2
E
E(+CO_2)
E+CO_2

FIG 8

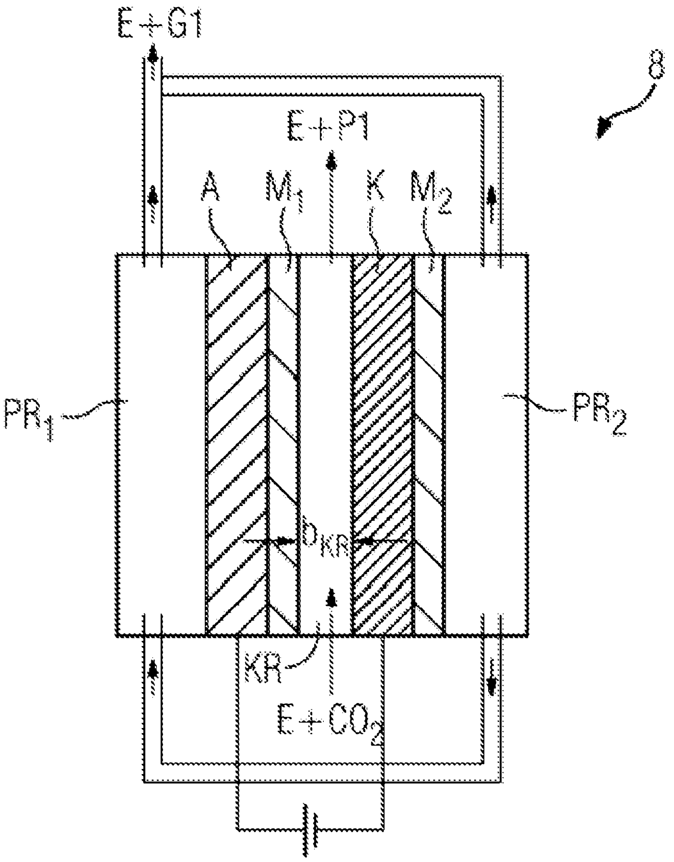
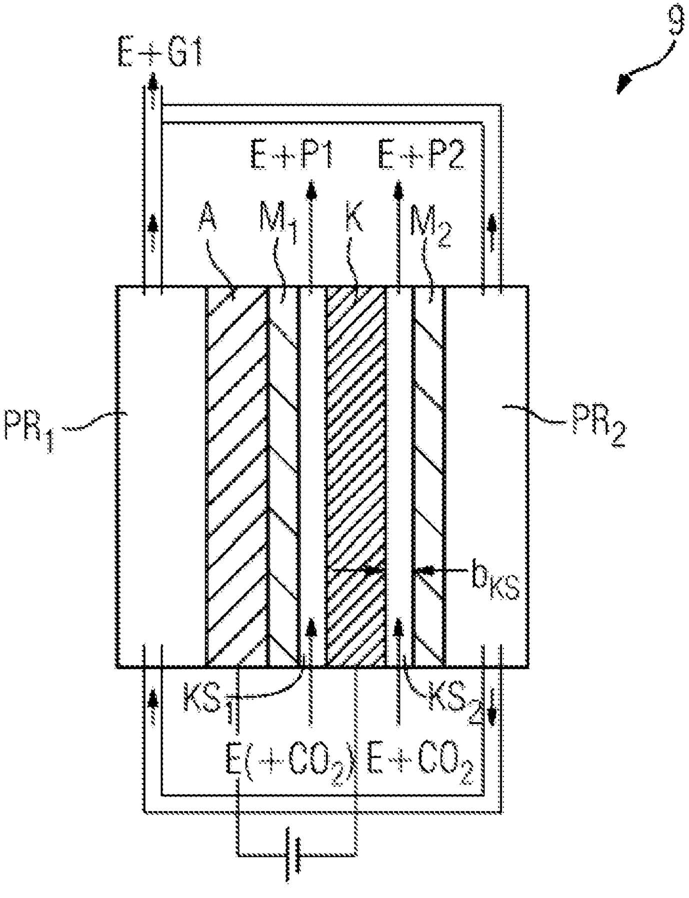

E+G1
8
E+P1
A
M1
K
M2
PR1
PR2
bKR
KR
E+CO2

FIG 9


E+G1
9
E+P1
E+P2
A
M1
K
M2
PR1
PR2
bKS
KS1
KS2
E(+CO2)
E+CO2