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(54) **REDUCTION METHOD AND ELECTROLYSIS SYSTEM FOR ELECTROCHEMICAL CARBON DIOXIDE UTILIZATION**

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(57) **ABSTRACT**

The present disclosure relates to electrochemical utilization of carbon dioxide. The teachings may be embodied in methods and electrolysis systems in which carbon dioxide is introduced into an electrolysis cell and reduced at a cathode. For example, a reduction method for carbon dioxide utilization by means of an electrolysis system may include: delivering carbon dioxide into a chamber containing a cathode; introducing a first material in the cathode chamber, enabling catalysis of a reduction reaction of carbon dioxide to a hydrocarbon compound or to carbon monoxide; and introducing a second material together with the electrolyte or a reactant/electrolyte mixture into the cathode chamber or metered separately into the cathode chamber. The second material enables cocatalysis of the reduction reaction by promoting charge transfer from the cathode to the first material. The first and second materials react with one another in situ as precursor and form hydrido-metal complexes or metal-carbonyl hydrides within the cathode chamber.

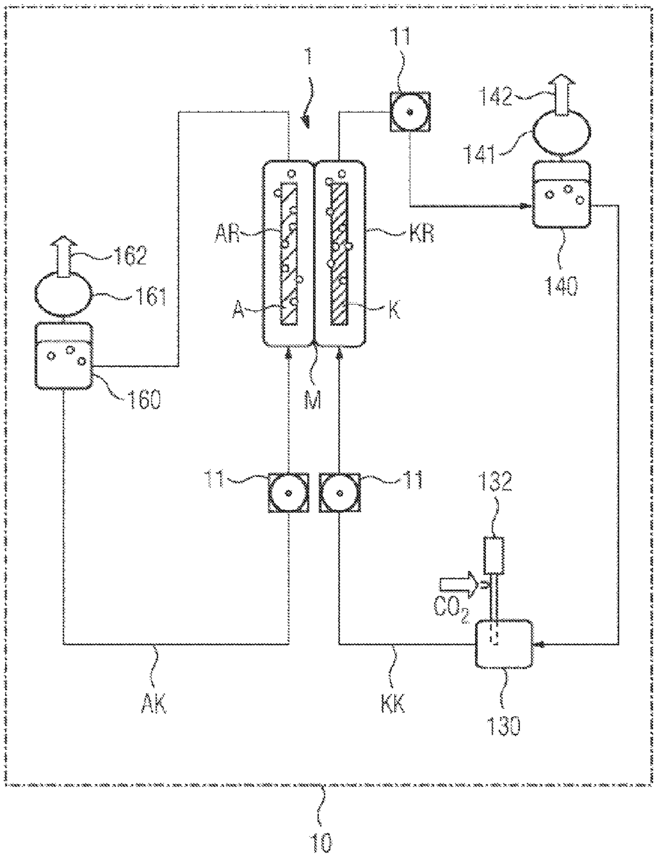


FIG 1

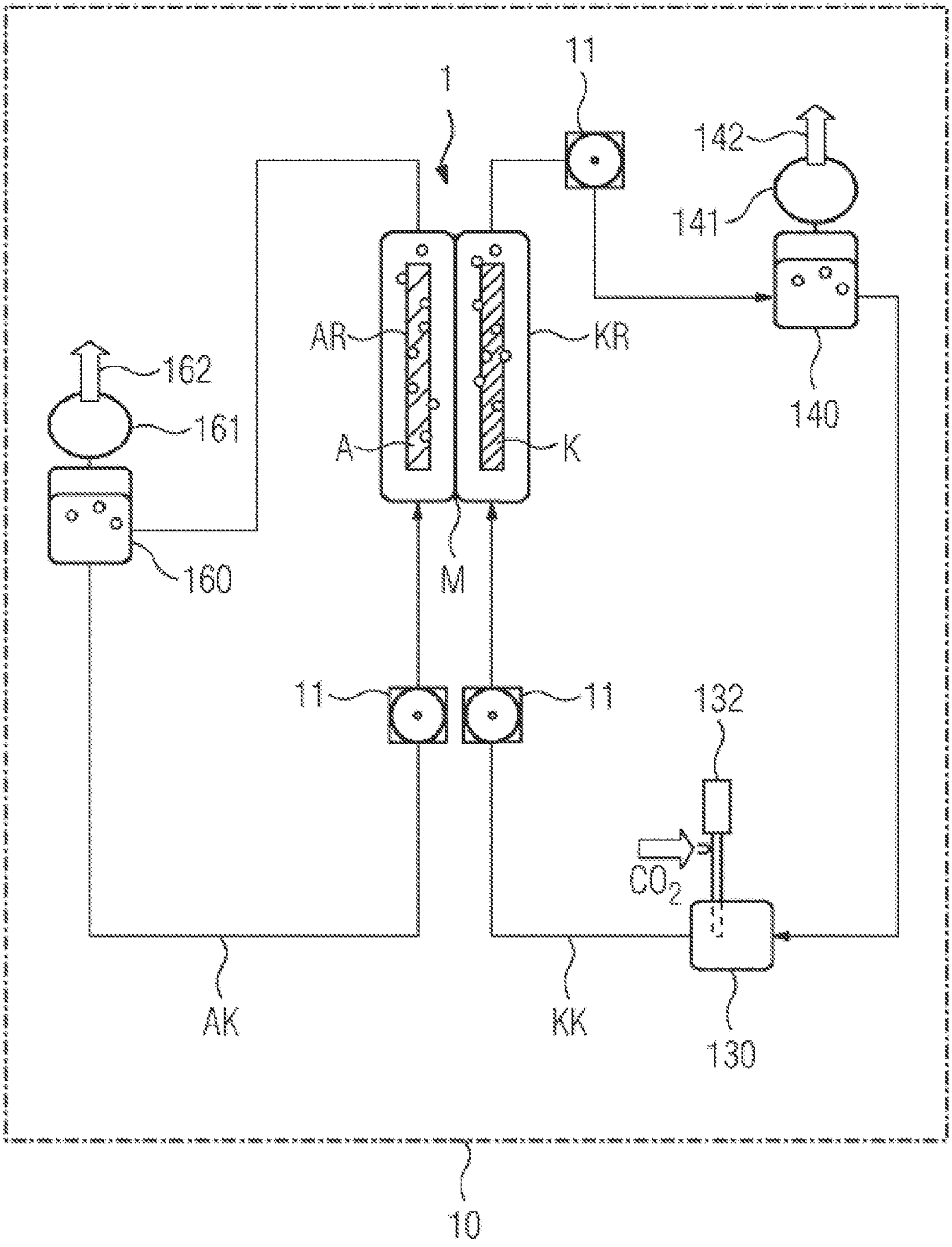


FIG 2

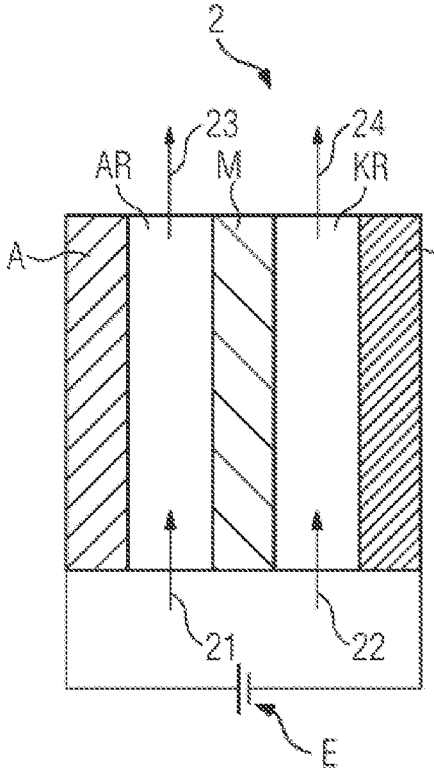


FIG 3

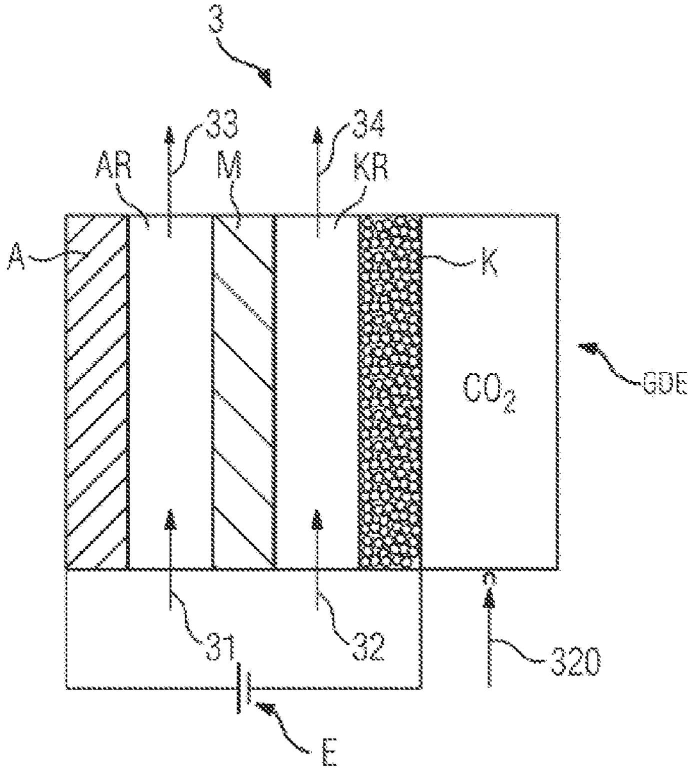


FIG 4

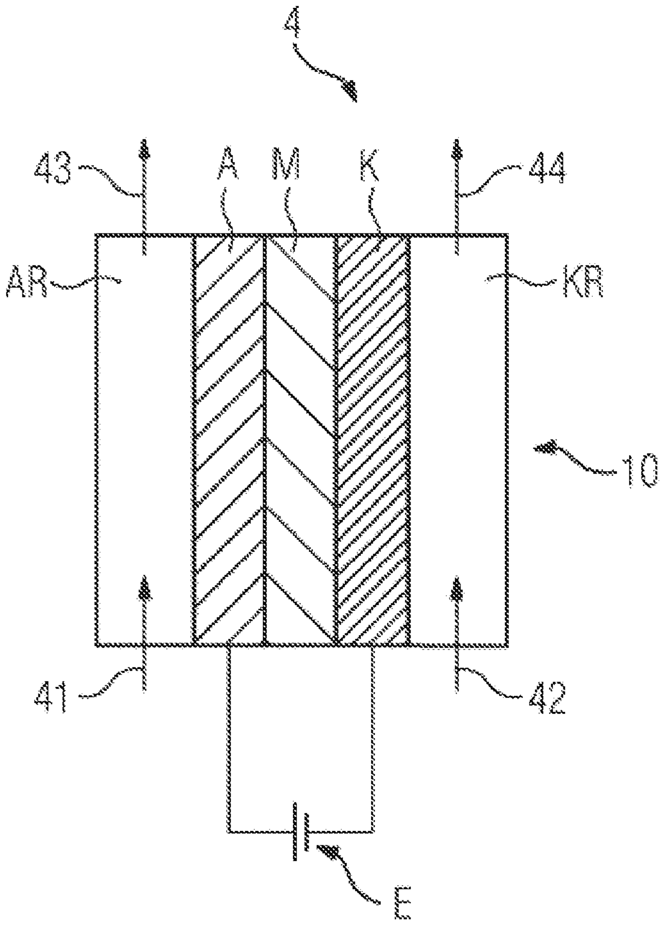


FIG 5
Prior Art

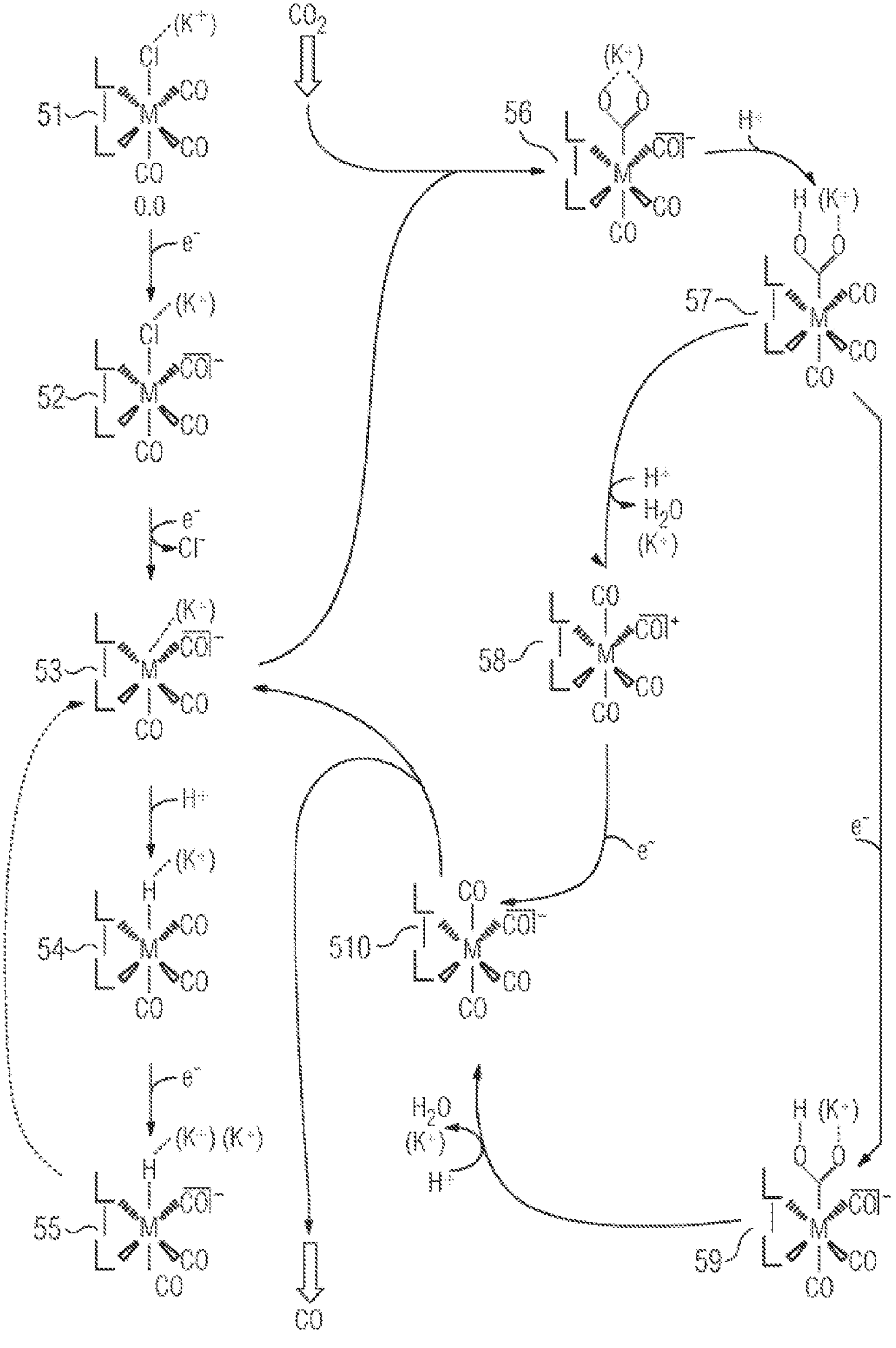


FIG 6

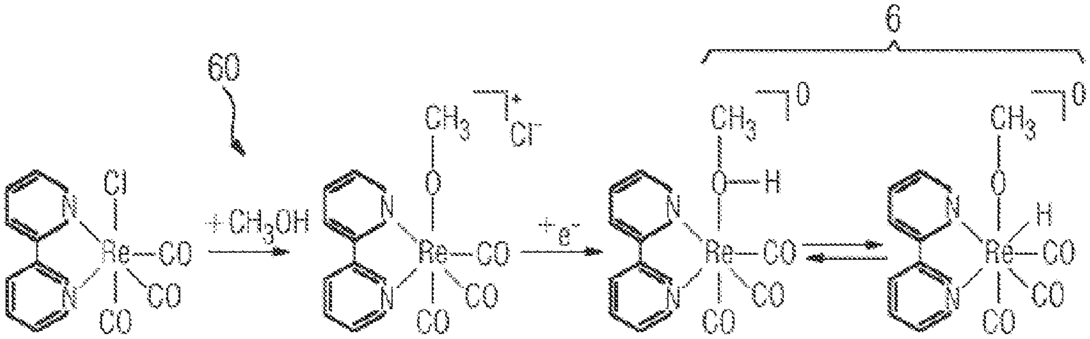

60
6
Cl
N
Re
CO
+ CH3OH
CH3
Cl−
O
+e−
O—H
H
0

FIG 7

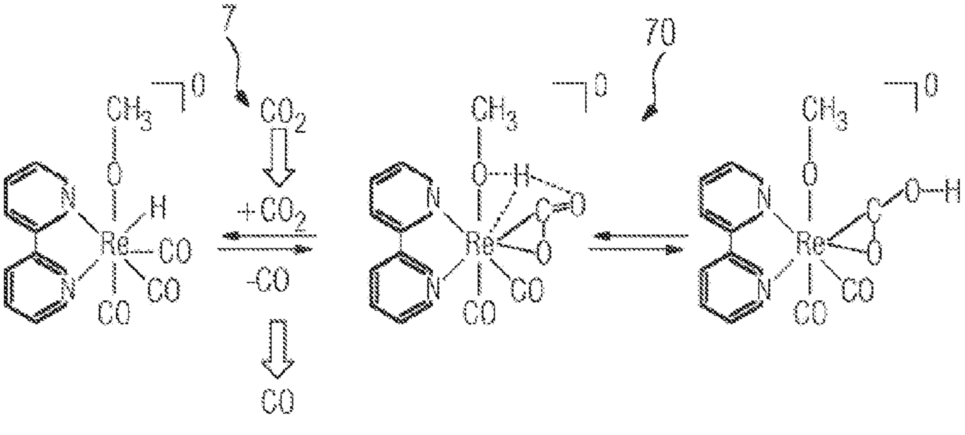

7
70
CO2
+CO2
-CO
CO
CH3
O
H
N
Re
C=O
O—H
0

FIG 8

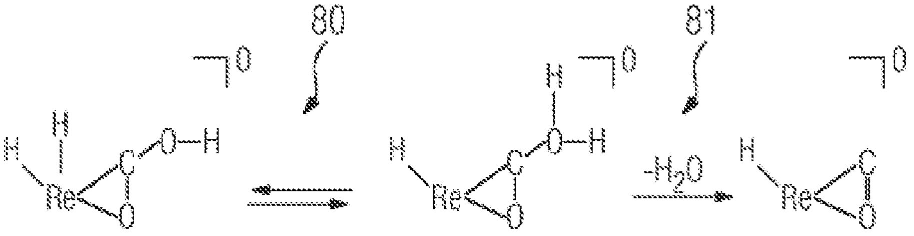


FIG 9

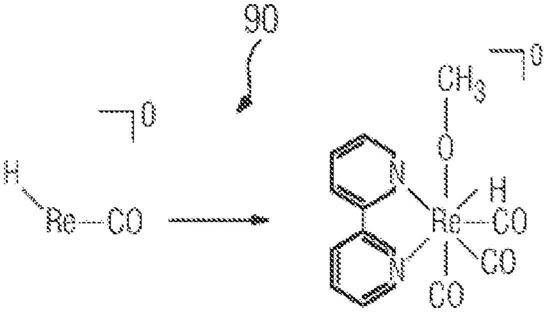


FIG 10

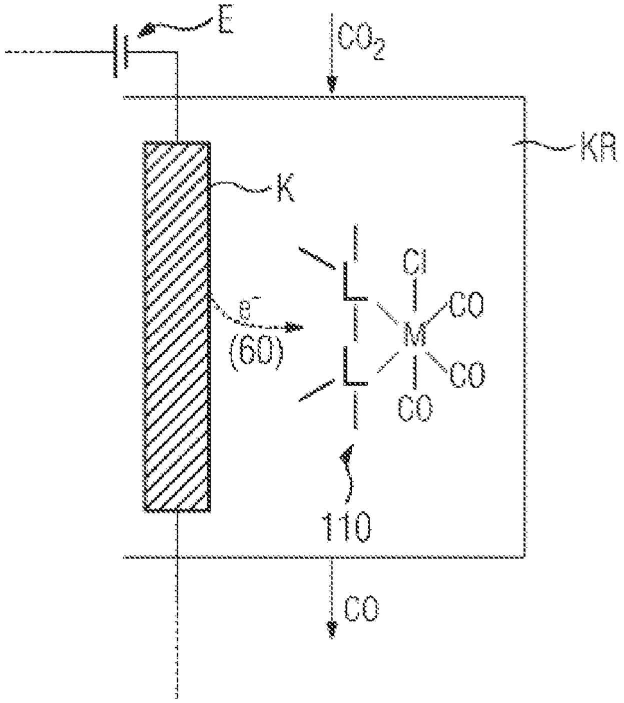


FIG 11

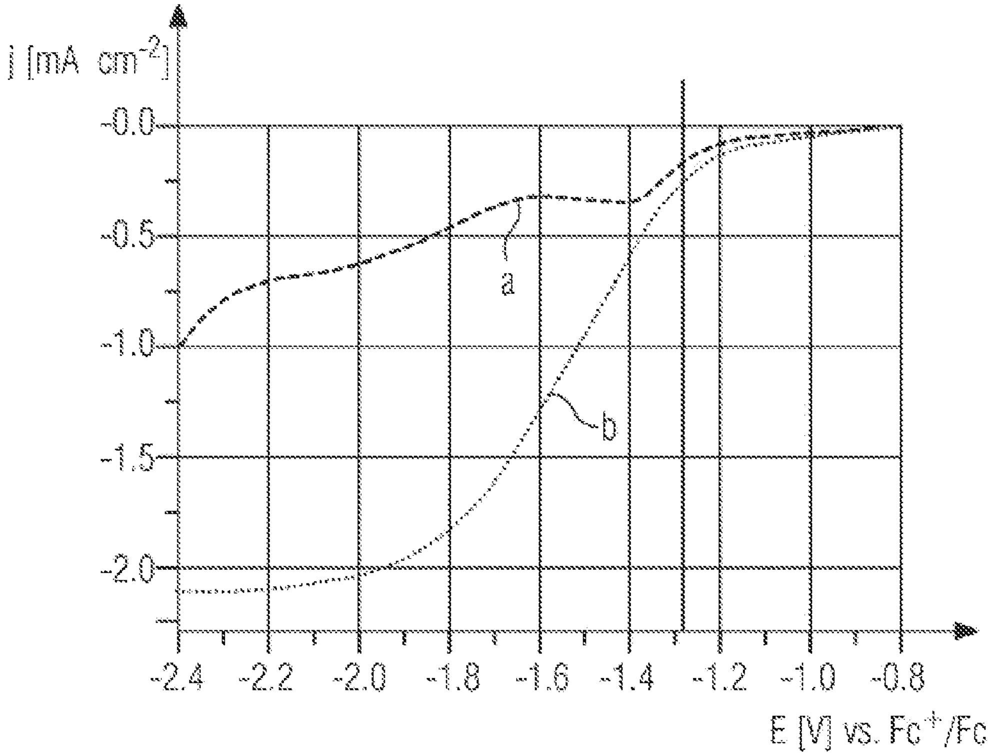

j [mA cm^{-2}]
-0.0
-0.5
-1.0
-1.5
-2.0
-2.4
-2.2
-2.0
-1.8
-1.6
-1.4
-1.2
-1.0
-0.8
E [V] vs. Fc$^+$/Fc
a
b

FIG 12

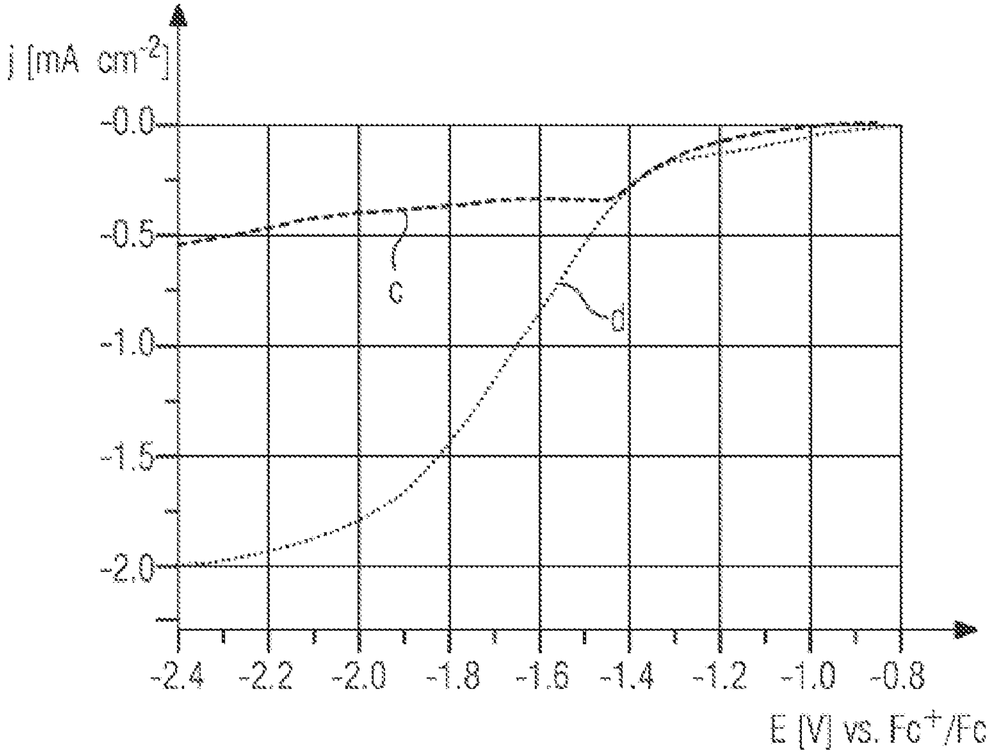
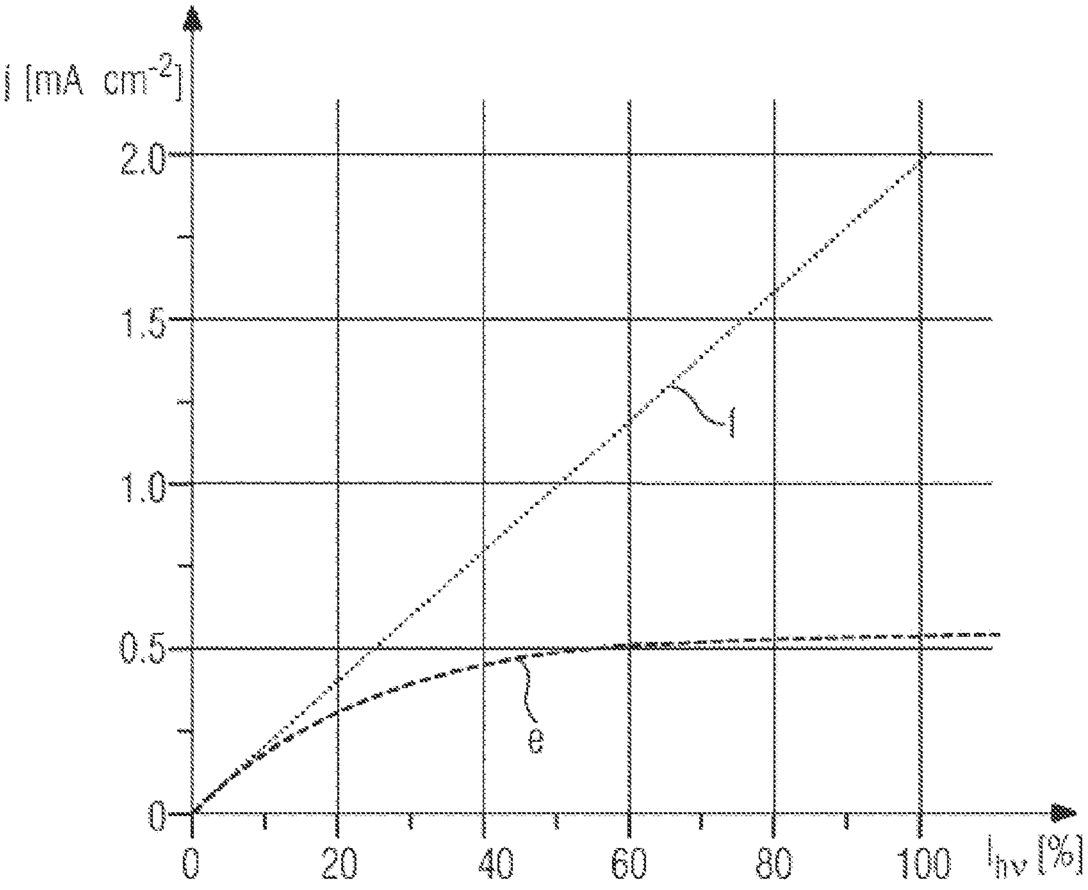

j [mA cm^{-2}]
-0.0
-0.5
-1.0
-1.5
-2.0
-2.4
-2.2
-2.0
-1.8
-1.6
-1.4
-1.2
-1.0
-0.8
E [V] vs. Fc$^+$/Fc
c
d

FIG 13



REDUCTION METHOD AND ELECTROLYSIS SYSTEM FOR ELECTROCHEMICAL CARBON DIOXIDE UTILIZATION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a U.S. National Stage Application of International Application No. PCT/EP2016/052516 filed Feb. 5, 2016, which designates the United States of America, and claims priority to DE Application No. 10 2015 202 258.7 filed Feb. 9, 2015, the contents of which are hereby incorporated by reference in their entirety.

TECHNICAL FIELD

[0002] The present disclosure relates to electrochemical utilization of carbon dioxide. The teachings may be embodied in methods and electrolysis systems in which carbon dioxide is introduced into an electrolysis cell and reduced at a cathode.

BACKGROUND

[0003] Currently around 80% of the worldwide energy demand is covered by the combustion of fossil fuels, the burning of which gives rise to worldwide annual emissions to the atmosphere of approximately 34,000 million tons of carbon dioxide. This release into the atmosphere contributes the majority of carbon dioxide, which in the case of a lignite power station, for example, can be up to 50,000 tons per day. Carbon dioxide is one of the gases known as greenhouse gases. While the extent of the negative effects on the atmosphere and the climate may be debated, reduction of emissions thereof is still sought. Since carbon dioxide occupies a very low position thermodynamically, it is difficult to reduce it to give reusable products. Thus, the actual recycling of carbon dioxide exists to date only within the realm of theory or of academia.

[0004] Natural breakdown of carbon dioxide is accomplished, for example, by photosynthesis. Photosynthesis is a process broken down temporally and, at a molecular level, spatially into numerous component steps. Carbon dioxide is reacted to form carbohydrates. This process cannot simply be adapted industrially. A replica of the natural photosynthesis process and using industrial photocatalysis has to date lacked adequate efficiency for use.

[0005] One known alternative is the electrochemical reduction of carbon dioxide. Systematic studies of the electrochemical reduction of carbon dioxide are still a relatively young field of development. First efforts to develop an electrochemical system to reduce an acceptable volume of carbon dioxide emerged only a few years ago. Laboratory-scale research efforts have shown that, preferentially, metals are to be used as catalysts for the electrolysis of carbon dioxide. 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, pp. 89-189, reveals Faraday efficiencies over various 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, the reaction products at a copper cathode comprise a multitude of hydrocarbons.

[0006] At a silver cathode, for example, predominantly carbon monoxide and a little hydrogen would be thus produced. The reactions at anode and cathode may be represented by the following reaction equations:

$$\text{Cathode: } 2CO_2+4e^-+4H^+\rightarrow 2CO+2H_2O$$

$$\text{Anode: } 2H_2O\rightarrow O_2+4H_++4e^-$$

Of particular interest economically, for example, is the electrochemical generation of carbon monoxide, methane, or ethene. These are products which in energetic terms are higher in value than carbon dioxide.

TABLE 1

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

[0007] The table reports Faraday efficiencies [%] of products formed in the reduction of carbon dioxide over various metal electrodes. The figures reported are valued for a 0.1 M potassium hydrogen carbonate solution as electrolyte.

[0008] For the purpose of promoting or accelerating reduction reactions of carbon dioxide, the prior art discloses catalysts, such as transition metal complexes and also transition metal-hydrido complexes, for example, as described for instance in the publication "Catalytic CO_2 Activation Assisted by Rhenium Hydride/$B(C_6F_5)_3$ Frustrated Lewis Pairs—Metal Hydrides Functioning as FLP Bases" by Y. Jiang, O. Blacque, T. Fox and H. Berke, published in J. Am. Chem. Soc., 2013, 135 (20), pages 7751-7760.

[0009] With regard to the functioning of such catalysts, FIG. **5** shows an exemplary process for a catalysis circuit. A complex, generally constructed from a central atom and one or more ligands, is able to pass through various oxidation states, and as it does so is able to place cations, electrons, OH groups or CO groups into solution or take them up again from solution. An example of catalytic reduction of carbon dioxide to carbon monoxide by means of a rhenium complex is also known from the publication "Elucidation of the Selectivity of Proton-Dependent Electrocatalytic CO_2 Reduction by fac-Re(bpy) $(CO)_3Cl$" by J. A. Keith, K. A. Grice, C. P. Kubiak and E. A. Carter, published in J. Am. Chem. Soc. 2013, 135, pages 15823-15829. In this regard it should be noted that it is not possible from the reaction conditions to predict whether at the end an inactive rhenium complex is formed, and therefore the catalytic activity is ended, or whether a reaction circuit will be formed. Any statements on this point from the prior art are speculative. Indeed, the publication by J. A. Keith et al. describes a theoretical mechanism in which the hydrido species in fact deactivates the catalyst.

SUMMARY

[0010] In contrast to the electrolysis of water, which has undergone further research and which can already be employed industrially, electrode solutions selected for the reduction of carbon dioxide have been costly, and in some cases act equally as electrode and as catalyst. For an industrially exploitable approach to carbon dioxide reduction, furthermore, the selection of electrodes must also consider their stability in the electrolyte environment.

[0011] Firstly, not every combination of electrode surface material, electrolyte and catalyst is capable of efficient reduction of carbon dioxide, since the charge transfer from the electrode to the catalyst is a limiting factor which must be borne in mind. Moreover, the predominantly pure metal electrodes used to date in the prior art for the electrochemical reduction of carbon dioxide are subject to alteration over time, in their morphology, for example, as a result of corrosion, for instance. Such alterations are brought about primarily in aqueous electrolytes. A move away from aqueous electrolytes, however, is an economic disadvantage for the catalysis.

[0012] An improved solution for the electrochemical utilization of carbon dioxide may avoid the disadvantages known from the prior art. In particular, the solution may not only allow effective depletion of carbon dioxide, but also specify economical utilization that is stable over the long term. Teachings of the present disclosure may be embodied in a reduction method for carbon dioxide utilization by means of an electrolysis system, wherein carbon dioxide (CO_2) is passed through a cathode chamber (KR) and brought into contact with a cathode (K). At least one first material is provided in the cathode chamber (KR) or is introduced into said chamber, said material enabling catalysis of a reduction reaction of carbon dioxide (CO_2) to at least one hydrocarbon compound or to carbon monoxide (CO). At least one second material, different from the first material, is introduced together with the electrolyte or a reactant/electrolyte mixture into the cathode chamber (KR) or metered separately into the cathode chamber, said second material enabling cocatalysis of the reduction reaction by promoting charge transfer from the cathode (K) to the first material. Second and first materials react with one another in situ as precursor and within the cathode chamber (KR) form hydrido-metal complexes or metal-carbonyl hydrides.

[0013] In some embodiments, the second material is a protic solvent. In some embodiments, the second material is water, methanol, ethanol or an alcohol.

[0014] In some embodiments, the first material is a complex, more particularly a metal complex. In some embodiments, the first material is a transition metal complex, more particularly having a heavy transition metal as central atom. In some embodiments, the first material is a metal carbonyl or metal carbonylate.

[0015] In some embodiments, first and second materials are stable in an aqueous environment.

[0016] In another example, the teachings of the present disclosure may be embodied in an electrolysis system for carbon dioxide utilization, comprising an electrolysis cell (**1**) having an anode (A) in an anode chamber (AR) and having a cathode (K) in a cathode chamber (KR). The cathode (K) has a layer in which the functions of a charge transfer layer and a surface protection layer are integrated. The cathode chamber (KR) is designed to accommodate carbon dioxide (CO_2) and bring it into contact with the cathode (K). The cathode chamber (KR) has a first material which enables catalysis of a reduction reaction of carbon dioxide (CO_2) to at least one hydrocarbon compound or to carbon monoxide (CO). The cathode chamber (KR) has a materials entry with a metering unit, via which at least one second material, different from the first material, can be introduced into the cathode chamber (KR), said second material enabling cocatalysis of the reduction reaction by promoting charge transfer from the cathode (K) to the first material.

[0017] In some embodiments, the cathode surface (K) has a work function whose energy level allows charge transfer to the first material.

[0018] In some embodiments, the cathode (K) comprises copper, copper oxide, TiO_2, or another metal oxide semiconductor material.

[0019] In some embodiments, the cathode (K) has a charge transfer layer whose surface has a work function whose energy level allows charge transfer to the first material.

[0020] In some embodiments, the cathode (K) is a photocathode.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] Examples and embodiments of the teachings of the present disclosure are described with reference to FIGS. **1** to **13** of the appended drawings:

[0022] FIG. **1** shows in diagrammatic representation an electrolysis system **10**, according to teachings of the present disclosure;

[0023] FIG. **2** shows in diagrammatic representation a two-compartment construction of an electrolysis cell, according to teachings of the present disclosure;

[0024] FIG. **3** shows in diagrammatic representation an electrolysis cell with a gas diffusion electrode, according to teachings of the present disclosure;

[0025] FIG. **4** shows in diagrammatic representation a PEM construction of an electrolysis cell, according to teachings of the present disclosure;

[0026] FIG. **5** shows a catalysis cycle for the reduction of carbon dioxide to carbon monoxide by means of a complex catalyst, according to teachings of the present disclosure;

[0027] FIG. **6** shows by way of example the addition of methanol as protic species to the catalyst rhenium-bipyridine, according to teachings of the present disclosure;

[0028] FIG. **7** shows proton transfer, using the catalyst rhenium-bipyridine as an example, according to teachings of the present disclosure;

[0029] FIG. **8** shows the renewed liberation of water as hydrogen source, according to teachings of the present disclosure;

[0030] FIG. **9** shows the final reaction for reverting to the original complex state, according to teachings of the present disclosure;

[0031] FIG. **10** shows diagrammatically the charge transfer from the cathode to a catalyst complex, according to teachings of the present disclosure;

[0032] FIG. **11** shows a current-voltage diagram of an exemplary electrolysis system having different electrode surfaces, according to teachings of the present disclosure;

[0033] FIG. **12** shows a further current-voltage diagram of an exemplary electrolysis system and the consequence of adding a protic species, according to teachings of the present disclosure; and

[0034] FIG. **13** shows a diagram in which the current density is plotted against the luminous intensity for a photo electrochemical electrolysis system, according to teachings of the present disclosure.

DETAILED DESCRIPTION

[0035] In the reduction methods disclosed herein for carbon dioxide utilization by means of an electrolysis system, carbon dioxide is passed through a cathode chamber and brought into contact with a cathode. At least one first material is provided in the cathode chamber or introduced into said chamber, said material enabling catalysis of a reduction reaction of carbon dioxide to at least one hydrocarbon compound or to carbon monoxide. At least one second material, which is different from the first material, is introduced into the cathode chamber, said second material enabling cocatalysis of the reduction reaction by promoting charge transfer from the cathode to the first material.

[0036] The cathode chamber of an electrolysis cell typically functions as a reaction space for the reduction of carbon dioxide; the cathode functions as a source of electrons. Besides the carbon dioxide as reduction reactant, the system may further comprise an electrolyte solution. Employed as the electrolyte, for example, is: a salt-containing, aqueous electrolyte, a salt-containing, organic solvent, an ionic liquid—and supercritical carbon dioxide as well can be employed as an electrolyte. For water-based electrolytes, preference is given to using potassium hydrogen carbonate $KHCO_3$ or potassium bromide KBr, potassium sulfate K_2SO_4 or potassium phosphate K_3PO_4 as salts. It is also possible for highly soluble salts of other cations to be used.

[0037] In some embodiments, the first material is either dissolved in the electrolyte and circulated accordingly in the electrolyte circuit, or is introduced separately from the electrolyte for reaction into the cathode chamber, or it is provided directly in the cathode chamber, for example in immobilized form on an internal surface of the cathode chamber or, more particularly, on the electrode surface, e.g. on the cathode surface.

[0038] The second material may be introduced together with the electrolyte or with a reactant/electrolyte mixture into the cathode chamber, or may be metered separately therefrom into the cathode chamber. The method described above may ensure high current density and, correspondingly, high yield in the carbon dioxide reduction, and of being energetically favorable and therefore competitive with other energy stores for volatile energy sources.

[0039] The first material is, for example, a complex, typically a metal complex in a low oxidation state, to which a hydrogen atom may be coordinated as ligand. Some embodiments use complexes which coordinate the hydrogen by protonation. This coordinated hydrogen then often has hydridic character and is therefore able to enter into reduction reactions. The proton source here constitutes the second material of the reduction system:

[0040] A protic solvent is typically employed as second material in the reduction method. A solvent is said to be protic if protons can easily be split off from molecules, which function as proton donors. Examples of protic solvents are water, alcohols, especially methanol and ethanol, mineral acids, or carboxylic acids, and also primary and secondary amines. In some embodiments, the second material is water, methanol, ethanol, or another alcohol. The resultant hydrides of the first material may be cocatalysts. An alternative second material used, for example, is a hydrido complex.

[0041] In some embodiments, the first material in the reduction method is, in particular, a metal complex. A complex here is a chemical compound composed of one or more central particles and also one or more ligands. In some embodiments, the first material comprises a metal complex with a relatively low oxidation state, which means that this complex has an electron-rich center, as in the case, for instance, of various transition metal complexes, with iron or cobalt as central atom, for example. In some embodiments, the first material comprises transition metal complexes with a heavy transition metal as central atom, such as molybdenum or rhenium, for example. A transition metal is said to be heavy when its atomic number is between 42 and 104. As first material for the reduction catalysis, it is also possible, alternatively, to use a metal carbonyl or metal carbonylate. Metal carbonyls are complex compounds of transition metals with at least one carbon monoxide ligand.

[0042] In the reduction method described, second and first materials may be selected such that they react with one another in situ, as precursors, and form hydrido-metal complexes or metal-carbonyl hydrides within the electrolysis system, or the cathode chamber, respectively. By means of the resultant hydrido-metal complexes or metal-carbonyl hydrides, the catalytic cycle of the reduction of carbon dioxide to at least one hydrocarbon compound or to carbon monoxide is driven very efficiently.

[0043] As already described, the hydrido fraction of the catalyst is especially significant for the catalysis of carbon dioxide reduction, since it allows particularly effective charge exchange with the cathode to take place. In the method, first and second materials employed may include materials which are also stable in an aqueous environment. Examples include many rhenium compounds, such as $ReH_3(OH)_3(H_2O)^-$, ReH_9^{2-}, and those which form in situ. “Stable” means that first and second materials do not split up into unwanted byproducts which counteract or damage the electrochemical reaction of carbon dioxide or, for example, the stability of the electrode system.

[0044] When selecting the materials it is also possible to ensure that the cathode is not attacked: for example, ions may be dissolved out of the surface of the electrode, or the surface of the electrode is even extensively destroyed in its morphology by corrosive attack. Unwanted byproducts may deposit on the cathode, for example, and thereby block the cathode in such a way that charge exchange would be hindered.

[0045] The electrolysis system for carbon dioxide utilization may comprise an electrolysis cell having an anode in an anode chamber and having a cathode in a cathode chamber. The design of the cathode chamber here is such that carbon dioxide can be accommodated and brought into contact with the cathode. The cathode chamber here has a first material through which it is possible to catalyze a reduction reaction of carbon dioxide to at least one hydrocarbon compound or to carbon monoxide.

[0046] Furthermore, the cathode chamber has a materials entry with a metering unit, via which at least one second material, which is different from the first material, can be introduced into the cathode chamber. By means of this second material, the reduction reaction can be cocatalyzed, by said second material promoting charge transfer from the cathode to the first material. Alternatively, the cathode chamber has a second material entry with a metering unit for the first material, or this material is caused to flow into the cathode chamber together with the electrolyte or with a reactant/electrolyte mixture. This electrolysis system may operate therein with a catalyst and a precisely meterable cocatalyst, thereby achieving a high current density and, accordingly, a high yield from the carbon dioxide reduction process.

[0047] The above-described electrolysis system for carbon dioxide utilization is notable, for example, for the fact that the cathode surface has a work function whose energy level allows charge transfer to the first material or is situated particularly favorably for this charge transfer, or the cathode surface has chemical properties which correspondingly promote charge transfer.

[0048] In the cathode chamber, the first material here is situated, for example, in dissolved form, in the electrolyte, for example, or is immobilized on the cathode surface or on another internal surface of the cathode chamber. In some embodiments, electrodes comprise platinum, copper, zinc, nickel, iron, titanium, zirconium, molybdenum, tungsten, or alloys thereof. The charge transfer here may also be interpreted chemically or in terms of semiconductor technology.

[0049] The cathode of the electrolysis system may include copper, copper oxide, titanium dioxide, or another metal oxide semiconductor material. The cathode may also be designed, for example, as a photocathode, which would allow a photoelectrochemical reduction process to be operated for the utilization of carbon dioxide—so-called photo assisted CO_2 electrolysis. In some embodiments, this system may also operate purely photocatalytically.

[0050] In some embodiments, the cathode (K) has a surface protection layer, for example. In some embodiments, semiconductor photocathodes and/or metallic cathodes may have a surface protection layer. By a surface protection layer is meant that a layer which is relatively thin in comparison to the overall electrode thickness separates the cathode from the cathode chamber. The surface protection layer for this purpose may comprise a metal, a semiconductor, or an organic material, e.g., a protective titanium dioxide layer. The protective effect is that the electrode is not attacked by the electrolyte or by reactants, products or catalysts, and their dissociated ions, in solution in the electrolyte, with consequent dissolving of ions from the electrode, for example. With regard specifically to the electrochemical reduction method in aqueous media, or at least in a medium which contains small quantities of water or of hydrogen, a suitable surface protection layer may provide long life and functional stability of the electrode in the process. Even small morphological changes, as a result of corrosive attacks, for example, may influence the overvoltages of hydrogen gas H_2 or carbon monoxide gas CO in aqueous electrolytes or water-bearing electrolyte systems. The consequence would be, on the one hand, a drop in the current density and, accordingly, a very low system efficiency for the conversion of carbon dioxide, and, secondly, the mechanical destruction of the electrode.

[0051] In some embodiments, the cathode has a charge transfer layer whose surface has a work function whose energy level allows charge transfer to the first material. This means that the cathode is able in terms of its predominant composition to rely on any other suitable material, and a charge transfer layer adapted to the first material in terms of its work function forms a suitable interface between cathode and electrolyte system with catalyst material. The focus in this case is especially on charge transfer to hydrido complexes. Suitable charge transfer layers of the cathode into the electrolyte or to the complex systems are, for example, thin precious metal coatings, semiconductor injection layers or else organic injection layers. The functions of the charge transfer layer and of the surface protection layer are preferably integrated in a single layer. This means that the charge transfer layer is responsible equally for the surface protection of the cathode, or the surface protection layer is selected such that it also does not hinder, or even such that it promotes, charge transfer.

[0052] The electrolysis system **10** shown diagrammatically in FIG. **1** first has, as a central element, an electrolysis cell **1**, here depicted in a two-compartment construction. An anode A is arranged in an anode chamber AR, and a cathode K in a cathode chamber KR. Anode chamber AR and cathode chamber KR are separated from one another by a membrane M. The anode chamber AR is attached with its electrolyte inlet and outlet to an anolyte circuit AK. Similarly, the cathode chamber KR is attached with its electrolyte and electrolysis-reactant inlet and its electrolyte and electrolysis-product outlet to a catholyte circuit KK.

[0053] The two circuits AK and KK each have at least one pump **11**, to convey the electrolyte and any reactants and products dissolved therein or mixed therewith through the electrolysis cell **1**. To introduce the carbon dioxide CO_2 into the catholyte circuit KK, said circuit may comprise, for example, an electrolyte container **130** having a carbon dioxide inlet **131** and also a carbon dioxide reservoir **132**. This construction ensures saturation of the electrolyte with carbon dioxide.

[0054] In some embodiments, the carbon dioxide is introduced into the electrolyte circuit via a gas diffusion electrode GDE. The directions of electrolyte flow in both circuits AK and KK are shown by means of arrows. After the cathode chamber KR in the circuit direction, the catholyte circuit KK preferably comprises a further pump **11**, which conveys the electrolyte, saturated with electrolysis products, into a container for gas separation **140**. Attached to this container is a product gas container **141** and, correspondingly, a product gas outlet **142**. Similarly, in the anolyte circuit AK, a container for gas separation **160** is integrated, which separates, for example, oxygen gas O_2 or, in the case of chloride-containing electrolytes chlorine gas from the electrolyte and allows them to be removed from the system via a product gas container **161** and the product gas outlet **162** attached thereto.

[0055] In some embodiments, the electrolysis system **10** may have an electrolysis cell construction as in one of the FIGS. **2** to **4** described below. In some embodiments, there is a gas diffusion electrode GDE, as shown in FIG. **3**. In that case, for the purpose of introducing the carbon dioxide CO_2 into the catholyte circuit KK, the gas diffusion electrode GDE comprises a carbon dioxide inlet **320**, and the cathode K is gas-permeable for the carbon dioxide CO_2, something which would render superfluous the carbon dioxide inlet **131** with the carbon dioxide reservoir **132**.

[0056] Each embodiment of the electrolysis cells **2**, **3** and **4** shown comprises at least one anode A in an anode chamber AR and also one cathode K in a cathode chamber KR. In some embodiments, anode chamber AR and cathode chamber KR are separated from one another at least by a membrane M. The membrane here may be an ion-conducting membrane, as for example an anion-conducting membrane or a cation-conducting membrane. The membrane may be porous layer or a diaphragm. The membrane may also ultimately be understood as a three-dimensional, ion-conducting separator, which separates electrolytes in anode and cathode chambers AR and KR.

[0057] Depending on the electrolyte solution used, some embodiments have not include membrane M. Anode A and cathode K are each connected electrically to a voltage supply E. The anode chamber AR of each of the electrolysis cells **2**, **3** and **4** shown is equipped in each case with an electrolyte inlet **21**, **31** and **41**. Similarly, each depicted anode chamber AR comprises an electrolyte outlet **23**, **33** and **43**, via which the electrolyte and also electrolysis byproducts formed at the anode, an example being oxygen gas O_2, are able to flow out of the anode chamber AR. The respective cathode chambers KR each have at least one electrolyte and product outlet **24**, **34** and **44**. The overall electrolysis product may be composed of a multiplicity of electrolysis products.

[0058] In some embodiments, such as in the two-compartment construction **2**, anode A and cathode K are separated from one another through anode chamber AR and cathode chamber KR by the membrane M. The electrodes, in what is called a polymer electrolyte membrane construction (PEM) **4** with porous electrodes, lie directly against the membrane M. As shown in FIG. **4**, there is a porous anode A and a porous cathode K. In the two-compartment construction **2** and also in the PEM construction **4**, the electrolyte and the carbon dioxide CO_2 are introduced into the cathode chamber KR via a common reactant inlet **22**, **42**.

[0059] In contradistinction to this, as shown in FIG. **3**, a so-called three-compartment construction **3**, in which the cathode chamber KR has an electrolyte inlet **32**, the carbon dioxide CO_2 is caused to flow separately therefrom into the cathode chamber KR via the cathode K of porous design. The porous cathode K may be configured as a gas diffusion electrode GDE.

[0060] A gas diffusion electrode GDE is characterized in that a liquid component, such as an electrolyte, and a gaseous component, such as an electrolysis reactant, can be brought into contact with one another in a pore system of the electrode, such as of the cathode K, for example. The pore system of the electrode here is designed such that the liquid phase and the gaseous phase equally may penetrate the pore system and be present simultaneously therein. For this purpose, typically, a reaction catalyst is porous in design and takes on the electrode function, or a porous electrode has catalytically acting components. For introducing the carbon dioxide CO_2 into the catholyte circuit KK, the gas diffusion electrode GDE comprises a carbon dioxide inlet **320**.

[0061] FIG. **5** shows a reaction circuit including: a complex **51**, generally constructed of central atom M and one or more ligands L, able to pass through various oxidation states **52**, and, in so doing, is able to place a cation K^+ or anion into solution or to take up the ion again from the solution or dispose it elsewhere in the complex **53**. On addition of carbon dioxide CO_2, indicated in FIG. **5** by an injecting arrow, an oxygen molecule may be transferred from the dioxide to the catalyst complex **56**.

[0062] Subsequently, in the reaction of the complex **57** to **58**, or else in another possible intermediate step via the complex **59**, water H_2O is then released, before the complex **510** gives up its CO group in the form of carbon monoxide CO and so reverts to the original state **53**, by means of which carbon dioxide CO_2 can then be converted again.

[0063] The take up of protons H^+ at one or other point in the circuit, and also the release of water H_2O, may be exploited for the reduction of carbon dioxide in accordance with the reduction method described. In FIG. **5**, K^+ is any desired cation, M is the central atom of the complex, e.g., a metal or transition metal atom, and L is a ligand, which may be, for example, a bipyridine ligand as in FIGS. **6** to **9**. Whether the complex in the state **53** reacts further to form the complex **56** or **54** is dependent, for example, on external conditions, such as the environment in which the complex is located, for example: the pH of the environment decides whether the hydrogen is present in dissociated form or bound to the complex. A complex **55** tends to be in an environment with an acid constant pK, of around 43, while a complex **59** tends to be present in an environment with an acid constant pK, of around 28—in other words, virtually never in water.

[0064] FIGS. **6** to **9** represent various chemical reactions may be included in the utilization method described. FIG. **6**, as an example of a first catalyst material, shows a rhenium-bipyridine complex Re(tBu-bipy) $(CO)_3CL$, which, accordingly at the beginning of the utilization method, must be present as starting material in the electrolysis cell **1** or must be introduced into said cell. The first reaction step **60** is the hydrogenation of this complex, e.g., the addition of hydrogen: in this example, methanol CH_3OH is added as the protic species. Uptake of a negative electrical charge e^- gives rise to the hydrido complexes shown on the right in FIG. **6**, which are mutually interconvertible via an equilibrium reaction and may therefore both be present in the electrolysis system **10**. In some embodiments, the symbol Re could be any desired metal, as an alternative to the bipyridine ligands shown, it would also be possible to use alternative ligands.

[0065] In FIG. **7**, on the left in the picture, the catalyzed reduction reaction **7** of carbon dioxide CO_2 to carbon monoxide CO is shown, in which the complex picks up an oxygen. Shown on the right in FIG. **7** is a further equilibrium reaction, which shows a cation transfer **70**. The charge transfer necessary for the reduction of carbon dioxide proceeds more readily through the hydridic catalyst complexes.

[0066] FIGS. **8** and **9** show the complexes in part without the appendant ligands. The central rhenium atom is again a suitable example, but again could be replaced by any metal atom M, e.g., another transition metal atom. The catalyst material is not consumed at this point, but is instead guided in a reaction circuit—that is, it reverts back to the original form of the hydrido complex **6**. Shown on the left in FIG. **8** is an equilibrium reaction between two oxidation states of the complex **80**. In a reduction reaction **80**, a water group is formed, which can be eliminated in the form of water H_2O in a further step **81**, shown on the right in FIG. **8**.

[0067] As shown in FIG. **9**, the original hydrido complex **6** is reproduced in this way. The step of water elimination **81** therefore represents a renewable hydrogen source in the system. By virtue of this additional proton source, the reaction rate of the reduction of carbon dioxide can be increased further, since the water H_2O can be reacted at the cathode K to give hydrogen H^+, H_2. This hydrogen H^+, H_2 need not automatically be present as hydrogen gas H_2 in the system, but instead may also be physisorbed or present in chemisorbed form on a surface in the electrolysis cell **1**. This allows, for example, a process of carbon dioxide reduction in nonaqueous electrolytes, which need merely be admixed with a small water fraction or hydrogen fraction that is enough to form hydrido complexes that drive the carbon dioxide catalysis.

[0068] FIG. **10** shows, by way of example and diagrammatically, a detail of an electrolysis cell **1**, specifically the cathode chamber KR with cathode K and connected voltage supply E. Additionally shown, in greatly simplified form, are arrows which point into and out of the cathode chamber KR, indicating carbon dioxide inlet and carbon monoxide outlet, and which are generally coincident with the electrolyte entry and electrolyte exit.

[0069] Alternatively to the carbon dioxide inlet via the electrolyte inlet into the electrolysis cell **1**, it would be possible here as well for the carbon dioxide CO_2 to be introduced again, in accordance with an embodiment as shown in FIG. **3**, into the cathode chamber KR through a gas diffusion electrode GDE. When an operating voltage E is present at the electrodes K, A of the electrolysis cell **1**, the cathode surface provides the reaction chamber with electrons e^-. The charge transfer from the cathode K to the catalyst complex **110** is indicated by an arrow **60**, which equally represents the hydrogenation reaction **60** as performed in FIG. **6**. This is intended to illustrate that the charge transfer from the cathode K to the catalyst complex **110** succeeds effectively only with the aid of an added protic species **60**. The protic species **60** in this case may be present together with the catalyst complex **110** in the electrolysis cell **1**, and conveyed through this cell via the electrolyte circuit, or metered specifically into the cathode chamber, via a separate metering unit, for example. The catalyst complex **110** may be present in solution in the electrolyte in the cathode chamber KR or may in particular be immobilized on the cathode surface.

[0070] FIGS. **11** to **13** show diagrams with measurement results which illustrate by way of example the effect of the method described. FIGS. **11** and **12** each show current-voltage diagrams of a linear sweep voltammetry measurement, in which a current density i [mA/cm^2] is plotted against a cell voltage E[V]. The voltage E applied to the electrodes is plotted in the diagrams **11** and **12** in each case against the ferrocene reference potential Fc^+/Fc, since the electrolyte solution used for this example is based on an acetonitrile solvent. With a linear course of the applied potential E in each case, different current profiles i are recorded: in the case of the first measurement, shown in FIG. **11**, the same conditions are present in each case for the electrolyte, and also for the catalyst complex **110** and the presence of a protic species **60**.

[0071] In this case, the first material used was the rhenium-bipyridine complex shown in FIGS. **6** to **9**, and the second material used was methanol. The dashed curve marked with a, for the lower current density i, was recorded without carbon dioxide CO_2 in the system. Instead, experimentally, the inert gas argon, Ar, was introduced into the electrolysis cell **1**. The absence of the carbon dioxide reduction reaction reduces the current flow i over the cathode K, correspondingly. The dotted curve, marked with b, whose current density value i climbs to more than double the first measurement a, was measured with the presence of carbon dioxide CO_2 in the cathode chamber KR.

[0072] For a system otherwise the same, in an equivalent measurement, the contribution of the cocatalyst methanol, CH_4O, was verified, by investigating a linear voltage course at the cathode with and without addition of methanol: the dashed curve c was recorded in the absence of the methanol cocatalyst; the dotted curve d, whose current density i climbs to just under four times the first measurement c without addition of methanol, was recorded with a one-molar concentration of methanol in the electrolyte solution, this being clear evidence of its cocatalytic effect.

[0073] Shown in FIG. **13**, finally, is a further example, in which a photoelectrode is used for the reduction of carbon dioxide. In FIG. **13**, accordingly, the current density i measured is shown as a function of the irradiated luminous intensity $I_{h\nu}$. The dashed curve e with the very low current density i, which also passes quickly into saturation, was measured for an electrolyte system without addition of a protic species **60**; the linear rise of the second, dotted measuring curve f was measured on addition of methanol CH_3OH at one-molar concentration.

What is claimed is:

1. A reduction method for carbon dioxide utilization by means of an electrolysis system, the method comprising:

delivering carbon dioxide into a cathode chamber containing a cathode;

introducing a first material in the cathode chamber, the first material enabling catalysis of a reduction reaction of carbon dioxide to a hydrocarbon compound or to carbon monoxide; and

introducing a second material, different from the first material, together with the electrolyte or a reactant/electrolyte mixture, into the cathode chamber or metered separately into the cathode chamber, said second material enabling cocatalysis of the reduction reaction by promoting charge transfer from the cathode to the first material;

wherein the first and second materials react with one another in situ as precursor and form hydrido-metal complexes or metal-carbonyl hydrides within the cathode chamber.

2. The reduction method as claimed in claim **1**, wherein the second material comprises a protic solvent.

3. The reduction method as claimed in claim **1**, wherein the second material is comprises a material selected from the group consisting of: water, methanol, ethanol, and alcohol.

4. The reduction method as claimed in claim **1**, wherein the first material comprises a metal complex.

5. The reduction method as claimed in claim **1**, wherein the first material comprises a transition metal complex.

6. The reduction method as claimed in claim **1**, wherein the first material comprises a metal carbonyl or metal carbonylate.

7. The reduction method as claimed in claim **1**, wherein the first and second materials are stable in an aqueous environment.

8. An electrolysis system for carbon dioxide utilization, the system comprising:

an electrolysis cell;

an anode in an anode chamber; and

a cathode in a cathode chamber;

wherein the cathode comprises a layer integrating the functions of a charge transfer layer and a surface protection layer;

wherein the cathode chamber accommodates carbon dioxide and brings carbon dioxide into contact with the cathode;

the cathode chamber includes a first material enabling catalysis of a reduction reaction of carbon dioxide to ahydrocarbon compound or to carbon monoxide;

the cathode chamber includes a materials entry with a metering unit, via which a second material, different from the first material, can be introduced into the cathode chamber; and

the second material enables cocatalysis of the reduction reaction by promoting charge transfer from the cathode to the first material.

9. The electrolysis system for carbon dioxide utilization as claimed in claim **8**, where a surface of the cathode has a work function whose energy level allows charge transfer to the first material.

10. The electrolysis system for carbon dioxide utilization as claimed in claim **8**, wherein the cathode comprises copper, copper oxide, TiO_2, or another metal oxide semiconductor material.

11. The electrolysis system for carbon dioxide utilization as claimed in claim **8**, wherein the cathode includes a charge transfer layer with a surface has having a work function whose energy level allows charge transfer to the first material.

12. The electrolysis system for photoelectrochemical carbon dioxide utilization as claimed in claim **8**, wherein the cathode comprises photocathode.

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