(19) DANMARK

(10) **DK/EP 3408429 T3**

Patent- og
Varemærkestyrelsen

(12)

Oversættelse af europæisk patentskrift

---

(51) Int.Cl.: *C 25 B 1/00 (2006.01)* *C 25 B 3/04 (2006.01)* *C 25 B 9/08 (2006.01)*
C 25 B 15/08 (2006.01)

(45) Oversættelsen bekendtgjort den: **2020-05-11**

(80) Dato for Den Europæiske Patentmyndigheds
bekendtgørelse om meddelelse af patentet: **2020-02-26**

(86) Europæisk ansøgning nr.: **17702563.2**

(86) Europæisk indleveringsdag: **2017-01-25**

(87) Den europæiske ansøgnings publiceringsdag: **2018-12-05**

(86) International ansøgning nr.: **EP2017051469**

(87) Internationalt publikationsnr.: **WO2017153081**

(30) Prioritet: **2016-03-10 DE 102016203946**

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

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

(72) Opfinder: **STARK, Katharina, Paul-Gordan-Strasse 19, 91052 Erlangen, Tyskland**
BALDAUF, Manfred, Am Kornfeld 52, 91056 Erlangen, Tyskland
HANEBUTH, Marc, Grünreuther Strasse 54, 90482 Nürnberg, Tyskland

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

(54) Benævnelse: **Fremgangsmåde og indretning til elektrokemisk udnyttelse af kuldioxid**

(56) Fremdragne publikationer:
US-A- 3 959 094
US-A- 4 673 473

Description

The present invention relates to a process and to an apparatus for electrical utilization of carbon dioxide. Carbon dioxide is introduced into an electrolysis cell and reduced at a cathode.

The demand for power varies significantly over the course of the day. There is also variation in the generation of power, with an increasing proportion of power from renewable energies during the course of the day. In order to be able to compensate for an oversupply of power in periods with a lot of sun and strong wind when demand for power is low, controllable power plants or storage means are required to store this energy.

One of the solutions currently being contemplated is the conversion of electrical energy to products of value which can especially serve as platform chemicals, especially ethene, methane or ethane, or synthesis gas which comprises carbon monoxide and hydrogen. One possible technique for conversion of electrical energy to products of value is electrolysis.

The electrolysis of water to hydrogen and oxygen is a method known in the prior art. But the electrolysis of carbon dioxide to carbon monoxide has also been a subject of research for a few years, and there are efforts to develop an electrochemical system that can reduce an amount of carbon dioxide in accordance with economic interests. At present, about 80% of global energy demand is covered by the combustion of fossil fuels, and the processes of combustion thereof cause global emissions of about 34 000 million tons of carbon dioxide into the atmosphere per year. Carbon dioxide is one of the “greenhouse gases”, the adverse effects of which on the atmosphere and the climate are a matter of discussion. Utilization of this carbon dioxide is therefore desirable.

US 4,673,473 and US 3,959,094 disclose apparatuses for the electrolysis of carbon dioxide.

An advantageous design of an electrolysis unit is a low-temperature electrolyzer in which carbon dioxide as product gas is metered into a cathode space with the aid of a gas diffusion electrode. The carbon dioxide is reduced to carbon monoxide at a cathode of the electrochemical cell, and water is oxidized to oxygen at an anode. Owing to diffusion limitations at the cathode, use of an aqueous electrolyte can result not only in the formation of carbon monoxide but also in the formation of hydrogen, since the water in the aqueous electrolyte is likewise electrolyzed. In the current state of the art, a maximum of 70% of the carbon dioxide used is electrochemically converted. Assuming a conversion level of carbon dioxide of 50% and noting that the Faraday efficiency for carbon monoxide and hydrogen is 50% in each case, the result is a product gas having a composition of carbon monoxide to hydrogen to carbon dioxide in a ratio of 1:1:1.

Being a product of value for storage of electrical energy, however, a minimum proportion of unconverted carbon dioxide in the product gas is desirable. Removal of the unconverted carbon dioxide is therefore necessary. This removal is disadvantageously energy-intensive.

It is therefore an object of the present invention to specify a process and an apparatus in which unconverted carbon dioxide can be separated in a low-energy manner from the product gas from an electrolysis unit.

The object is achieved by a process according to claim 1 and an apparatus according to claim 8.

The process of the invention for electrochemical utilization of carbon dioxide comprises the following steps: first of all, a carbon dioxide electrolysis cell having a first anode space and a first cathode space is provided, where the first anode space and the first cathode space are separated by a first membrane, where a cathode is arranged within the first cathode space such that it separates a first cathode subspace and a second cathode subspace, where the first cathode subspace adjoins the first membrane. Subsequently, the first electrolyte is guided as first catholyte into the first cathode subspace. The carbon dioxide is guided into the second cathode subspace. In the second cathode subspace, the carbon dioxide is reduced to a first product gas. The first product gas leaves the carbon dioxide electrolysis cell separately from the first catholyte that has been basified during the reduction of the carbon dioxide. Downstream of the carbon dioxide electrolysis cell, the first product gas and the basic first catholyte are combined. The non-reduced carbon dioxide is then separated from the first product gas by means of the basic first catholyte as absorbent.

The apparatus for electrical utilization of carbon dioxide comprises a carbon dioxide electrolysis cell for reducing carbon dioxide to a first product gas, where the carbon dioxide electrolysis cell has a first anode space and a first cathode space, where a membrane is arranged between the first anode space and the first cathode space and where a two-dimensional cathode in the first cathode space separates a first cathode subspace from a second cathode subspace, where the first cathode subspace adjoins the first membrane. In addition, the apparatus comprises a first conduit into the second cathode subspace for guiding the carbon dioxide into the second cathode subspace. In addition, the apparatus comprises a second conduit into the second cathode subspace for guiding a first electrolyte as the first catholyte. A fourth conduit leads from the first cathode subspace into a gas scrubbing apparatus for guiding the basic first catholyte. A fifth conduit leads from the second cathode subspace to the gas scrubbing apparatus for guiding the first product gas and the carbon dioxide not reduced in the carbon dioxide electrolysis cell. In addition, the apparatus comprises a gas scrubbing apparatus for separating the non-reduced carbon dioxide from the first product gas by means of the first catholyte.

What is advantageously exploited in the process of the invention and the apparatus of the invention is that there is a change in the pH of the catholyte and also of an anolyte in the carbon dioxide electrolysis cell. If an aqueous electrolyte comprising a conductive salt, especially potassium sulfate or an ammonium salt, is used in the carbon dioxide electrolysis, there is predominant transport of potassium ions rather than hydrogen ions through the membrane in the electrolysis. The protons remaining in the anolyte, in the absence of buffer capacity of the anolyte, lead to significant lowering of the pH. There is also a change in the pH in the catholyte. As a result of the guiding of the carbon dioxide within the second cathode subspace without direct contact with the catholyte in the first cathode subspace, there is no carbonate equilibrium in the catholyte that would be established directly in the case of guiding of the carbon dioxide through the catholyte. The buffer effect of the potassium hydrogencarbonate according to equation 1 thus cannot take place. There is accumulation of the hydroxide ions that arise as a result of the reduction of carbon dioxide, or water in the case of the side reaction, such that there is a rise in the pH of the catholyte, i.e. it becomes basic.

$$K^{+} + OH^{-} + CO_2 \rightarrow KHCO_3 \qquad \text{(EQ 1)}$$

If the basified catholyte and the product gas are then combined with the non-reduced carbon dioxide in a gas scrubbing apparatus, the basic catholyte acts as absorbent for the carbon dioxide and absorbs it from the gas phase. The product gas, which especially comprises carbon monoxide and the hydrogen formed from the water in the aqueous electrolyte in an electrochemical side reaction, has now been freed of carbon dioxide.

The absence of the buffer effect of the carbon dioxide in the first cathode subspace itself advantageously results in distinct boosting of the pH effect, and so the pH becomes strongly basic. The combining of the basic electrolyte with the product gas contaminated with unreacted carbon dioxide in the gas scrubbing apparatus then advantageously leads to very effective absorption of the carbon dioxide into the catholyte as absorbent. By virtue of the catholyte and the product gas to be cleaned being guided separately from the carbon dioxide electrolysis cell into the gas scrubbing apparatus, a thermodynamic equilibrium is advantageously not established until within the gas scrubbing apparatus. This results in a distinct increase in the quality of the separation by comparison with guiding them together. This leads to an energy-optimized process. This purification of the product gas is thus advantageously possible in a very low-energy manner, since the use of energy-intensive heating or cooling apparatuses is avoided. Particularly advantageously, the supply of an additional absorbent is avoided here. The absorbent can additionally be regenerated very easily, such that the bound carbon dioxide is released again and can be reused in the process. Advantageously, the process is thus very favorable from an economic standpoint as well. Energy is also saved because the avoidance of the additional absorbent means that further separation steps are dispensed with.

The separation of the catholyte from the product and reactant gas is possible since the carbon dioxide is run past the cathode in the second cathode subspace separately from the catholyte present in the first cathode subspace. The reaction of the carbon dioxide to give carbon monoxide takes place at the cathode in contact with the catholyte. As a result of a small pressure differential between the carbon dioxide and the catholyte, the relative pressure of the carbon dioxide being somewhat greater, the catholyte remains virtually entirely within the first cathode subspace. Typically, the gaseous components of the reaction then leave the electrolysis cell via an outlet from the second cathode subspace, and the catholyte via an outlet from the first cathode subspace.

Particularly advantageously, the pH effect of the catholyte and the anolyte can be assisted by adjusting the pumped circulation rate of the electrolyte to a low dwell time in the carbon dioxide electrolysis cell. This further increases the pH differential of anolyte and catholyte.

A rise in the pH of the catholyte can also be increased via the selection of the operating parameters and via a suitable design of the carbon dioxide electrolysis cell. Possible adjustment parameters for increasing the rise in pH of the catholyte may be: the geometry of the electrolysis cells, the gap width in the cathode space between the cathode and the membrane, the transport resistances of the ions in aqueous solution via selection of the conductive salt, and the availability of carbon dioxide at the cathode.

Advantageously, the unconverted carbon dioxide is absorbed in the gas scrubbing apparatus. It is also possible here to guide the basic catholyte and the product gas from the two separate conduits into a common conduit, such that the absorption takes place directly within this common conduit. In this case, the gas scrubbing apparatus accordingly merely takes the form of a conduit, in which case further configurations for improvement of the mixing of the two phases are appropriate, more particularly a static mixer.

In an advantageous configuration and development of the invention, the first electrolyte is guided from a regeneration vessel as a first anolyte into the anode space. The pH effect is advantageously assisted when the first electrolyte is used both as first catholyte and as first anolyte. Appropriately, a third conduit leads from the regeneration vessel into the first anode space.

In a further advantageous configuration and development of the invention, downstream of the electrolysis cell and the gas scrubbing apparatus, the catholyte and the anolyte are combined in the regeneration vessel in order to rebalance the ever-increasing discrepancy between the pH of the cathode side and the anode side. For instance, it is advantageously possible to conduct a steady-state electrolysis process with a constant pH in the regeneration vessel. Advantageously, the use of an additional absorbent in this process is avoided. In the regeneration vessel, the carbon dioxide bound is released again and the pH is regenerated again at the same time. Regeneration is understood here to mean balancing of the pH of the first catholyte and the first anolyte. More particularly, the pH after a regeneration is 8 to 10.

Appropriately, the apparatus in that case comprises an eighth conduit from the gas scrubbing apparatus to the regeneration vessel for guiding the first catholyte, and a ninth conduit from the first cathode space into the regeneration vessel.

In a further advantageous configuration and development of the invention, the product gas comprises carbon monoxide and/or ethene and/or methane and/or ethane. Advantageously, these products can be used as starting material for chemical syntheses. Advantageously, carbon dioxide is thus electrochemically converted to a material of value.

In a further advantageous configuration and development of the invention, the carbon dioxide released in the regeneration vessel is returned to the carbon dioxide electrolysis cell as reactant. Advantageously, the degree of CO_2 utilization of the carbon dioxide electrolysis cell is thus increased, since the carbon dioxide which has not been converted in a first cycle can be converted in the next cycle.

In an advantageous configuration and development of the invention, the electrolyte used is a electrolyte comprising potassium and/or ammonium, especially a potassium sulfate. These electrolytes advantageously increase the conductivity of the catholyte or anolyte with virtually unchanged pH-buffering properties. They therefore enable the migration of the protons across the membrane and hence also the changing of the pH of the anolyte and of the catholyte in the respective anode or cathode space. Further substance classes are likewise usable as electrolytes. More particularly, the alkali metals lithium, sodium, rubidium or cesium may also be used as electrolyte. Anions used in the electrolyte or conductive salt may especially be halides or phosphates.

In a further advantageous configuration and development of the invention, the apparatus comprises a sixth conduit to the regeneration vessel to an inlet in the second cathode subspace in order to return the carbon dioxide from the regeneration vessel to the carbon dioxide electrolysis cell.

In a further advantageous configuration and development of the invention, the cathode is a gas diffusion electrode. With the gas diffusion electrode, it is particularly advantageously possible to allow the reaction of the carbon dioxide reactant gas with the liquid catholyte to proceed at the surface of the electrode and then to guide gas and liquid phases out of an electrolysis cell separately from one another.

In a further advantageous configuration and development of the invention, the gas scrubbing apparatus comprises random packings or a structured packing. These internals advantageously increase the interface between the carbon dioxide to be removed and the absorbent, i.e. the catholyte, which means that the thermodynamic equilibrium can be more quickly established. Spraying of the absorbent in a gas phase is likewise conceivable in order to maximize the surface area between the two phases.

Further configurations and further features of the invention are elucidated in detail by the figures which follow. These are purely illustrative configurations and combinations of features that do not mean any restriction of the scope of protection. Features having the same mode of action and the same designation but in different configurations are given the same reference numerals.

The figure shows:

Figure 1 a carbon dioxide electrolysis cell with a gas scrubbing apparatus and two separate conduits.

In this working example, the electrolysis apparatus 1 comprises a carbon dioxide electrolysis cell 2. The carbon dioxide electrolysis cell 2 comprises a first membrane 5 to which a first anode 9 has been applied directly. The membrane 5 divides the electrolysis cell into a first anode space 3 and a first cathode space 4. The first cathode 6 is arranged between a first cathode subspace 7 and a second cathode subspace 8. The first cathode 6 completely separates these two spaces from one another. More particularly, the first cathode 6 is two-dimensional in order to completely separate the two cathode subspaces 7 and 8 from one another.

There is an aqueous electrolyte EL in a regeneration vessel 10. This aqueous electrolyte EL typically comprises a salt, especially potassium sulfate K_2SO_4 or potassium hydrogencarbonate $KHCO_3$. The aqueous electrolyte may alternatively comprise sulfates, hydrogencarbonates or phosphates. In this example, the aqueous electrolyte EL comprises 1 mol/L potassium hydrogencarbonate.

Carbon dioxide CO_2 is guided via a first conduit 11 into the second cathode subspace 8. A first catholyte K1 is guided out of the regeneration vessel 10 into the first cathode subspace 7. A further proportion of this electrolyte EL is guided as first anolyte A1 via a third conduit 13 into the first anode space 3. Appropriately, the carbon dioxide electrolysis cell 2 has a voltage source.

During the electrolysis, the carbon dioxide CO_2 is reduced at the first cathode 6 to carbon monoxide CO. The first cathode 6 is typically a gas diffusion electrode. The catholyte K1 from the first cathode subspace 7 can preferably enter the gas diffusion electrode in contact with the carbon dioxide CO_2 to be reduced. Water is oxidized to oxygen at the first anode 9. Currently only 30% to 70% of the carbon dioxide CO_2 is electrochemically converted. Therefore, the product gas PG comprises both carbon monoxide CO and non-reduced carbon dioxide CO_2.

After the electrolysis, the product gas is guided via the fifth conduit 15 into a gas scrubbing apparatus 32. The first catholyte K1 is guided via a fourth conduit from the carbon dioxide electrolysis cell 2 to the gas scrubbing apparatus 32. The first catholyte K1 and product gas PG are guided separately from one another. In the gas scrubbing apparatus 32, the gas and the liquid phase are brought into contact with one another. In order to increase the mass transfer between the phases, the gas scrubbing apparatus 32 can advantageously be filled with random packings or comprise a structured packing. In addition, spraying of the first catholyte K1 into the product gas PG is possible.

In the gas scrubbing apparatus 32, the basic catholyte K1 is used as absorbent for the non-reduced carbon dioxide CO_2. The separate guiding of the basic first catholyte K1 and the product gas PG results in establishment of a thermodynamic equilibrium only once they are within the gas scrubbing apparatus 32. In this case, the non-reduced carbon dioxide CO_2 is enriched in the catholyte K1. The catholyte K1 enriched with carbon dioxide CO_2

then leaves the gas scrubbing apparatus 32 via an eighth conduit 18 and returns to the regeneration vessel 10.

Oxygen, the anode gas formed at the first anode A1, leaves the anode space 3 via a tenth conduit 20 for a second removal apparatus 33. In the second removal apparatus 33, the oxygen O_2 is separated from the anolyte A1. The oxygen leaves the electrolysis apparatus 1 via a twelfth conduit 35. The first anolyte A1 is returned to the regeneration vessel 10 via a ninth conduit 19. The product gas PG leaves the electrolysis apparatus 1 via a thirteenth conduit 36.

In the regeneration vessel 10, the first anolyte A1 and the first catholyte K1 are regenerated. This especially establishes a pH within a range between 8 and 10. The bound carbon dioxide CO_2 is released during the regeneration from the first catholyte K1 and can be returned to the electrolysis cell 2 via a sixth conduit 16. The regenerated electrolyte EL is subsequently returned back to the anode space and cathode space 7, 8 as first catholyte K1 and second anolyte A1.

Patentkrav

1. Fremgangsmåde til elektrokemisk udnyttelse af kuldioxid (CO_2) omfattende de følgende trin:
- tilvejebringelse af en kuldioxid-elektrolysecelle (2) med et første anoderum (3) og et første katoderum (4), hvor det første anoderum (3) og det første katoderum (4) adskilles af en første membran (5), hvor en første katode (6) er anbragt i det første katoderum (4) på en sådan måde, at den adskiller et første katodedelrum (7) og et andet katodedelrum (8), hvor det første katodedelrum (7) grænser op til den første membran (5),
- føring af en første elektrolyt (EL) som første katolyt (K1) ind i det første katodedelrum (7),
- føring af kuldioxidet (CO_2) ind i det andet katodedelrum (8),
- reducering af kuldioxidet (CO_2) til en første produktgas (PG) i det andet katodedelrum (8),
- at føre den første katolyt (K1) ud af det første katodedelrum (7) og produktgassen (PG) ud af det andet katodedelrum (8) adskilt fra hinanden,
- sammenføring af den første produktgas (PG) og den første katolyt (K1) efter kuldioxid-elektrolysecellen (2),
- fraseparering af ikke reduceret kuldioxid (CO_2) fra den første produktgas (PG) ved hjælp af den første katolyt (K1) som absorptionsmiddel.

2. Fremgangsmåde ifølge krav 1, hvor den første produktgas (PG) og den første katolyt (K1) sammenføres i en gasvaskeindretning (32).

3. Fremgangsmåde ifølge et af kravene 1 eller 2, hvor den første elektrolyt (EL) også som en første anolyt (A1) føres ind i anoderummet (3) fra en regenerationsbeholder (10).

4. Fremgangsmåde ifølge krav 3, hvor den første katolyt (K1), der under reduktionen af kuldioxidet (CO_2) er blevet basisk, og den første anolyt (A1), der under reduktionen af kuldioxidet (CO_2) er blevet sur, føres tilbage til regenerationsbeholderen (10).

5. Fremgangsmåde ifølge et af de foregående krav, hvor produktgassen (PG) omfatter carbonmonoxid (CO) og/eller ethen og/eller methan og/eller ethan.

6. Fremgangsmåde ifølge et af kravene 3 til 5, ved hvilken kuldioxidet (CO_2), som frigives i regenerationsbeholderen (10), føres tilbage til kuldioxid-elektrolysecellen (2).

7. Fremgangsmåde ifølge et af de foregående krav, hvor der som elektrolyt (EL) anvendes en elektrolyt (EL), der omfatter kalium og/eller ammonium, især et kaliumsulfat.

8. Indretning (1) til elektrokemisk udnyttelse af kuldioxid (CO_2) omfattende:
- en kuldioxid-elektrolysecelle (2) til reducering af kuldioxid (CO_2) til en første produktgas (PG), hvor kuldioxid-elektrolysecellen (2) omfatter et første anoderum (3) og et første katoderum (4), hvor der mellem det første anoderum (3) og det første katoderum (4) er anbragt en første membran (5), og hvor en flad katode i det første katoderum (4) adskiller et første (7) fra et andet katodedelrum (8), hvor det første katodedelrum (7) grænser op til den første membran (5),
- en første ledning (11) ind i det andet katodedelrum (8) til føring af kuldioxidet (CO_2) ind i det andet katodedelrum (8),
- en anden ledning (12) ind i det første katodedelrum (7) til føring af en første elektrolyt (EL) som første katolyt (K1),
- en fjerde ledning (14) fra det første katodedelrum (7) ind i en gasvaskeindretning (32) til føring af den første katolyt (K1),
- en femte ledning (15) fra det andet katodedelrum (8) til gasvaskeindretningen (32) til føring af den første produktgas (PG) med ikke reduceret kuldioxid (CO_2) separat fra den første katolyt (K1) ind i gasvaskeindretningen (32),
- gasvaskeindretningen (32) til fraseparering af det ikke reducerede kuldioxid (CO_2) fra den første produktgas (PG) ved hjælp af den første katolyt (K1).

9. Indretning (1) ifølge krav 8 med en tredje ledning (13) fra en regenerationsbeholder (10) ind i det første anoderum (3) til føring af den første elektrolyt

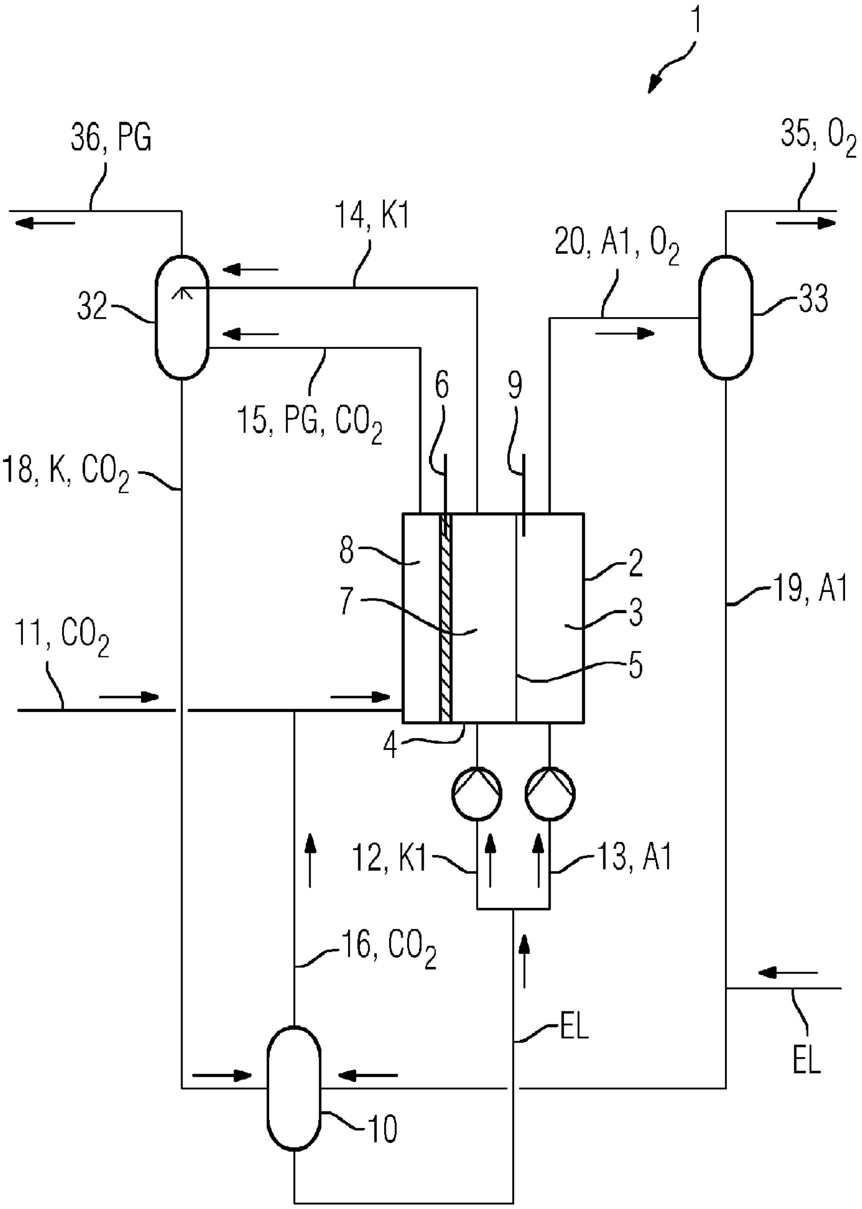
(EL) som første anolyt (A1) og den anden ledning (12) fra regenerationsbeholderen (10) ind i det første katodedelrum (7).

10. Indretning (1) ifølge krav 9 med en ottende ledning (18) fra gasvaskeindretningen (32) til regenerationsbeholderen (10) til føring af den første katolyt (K1) og/eller en niende ledning (19) fra anoderummet (3) ind i regenerationsbeholderen (10) til føring af den første anolyt (A1).

11. Indretning (1) ifølge et af kravene 9 eller 10 med en sjette ledning (16) fra regenerationsbeholderen (10) til en indgang af det andet katodedelrum (8) til tilbageførsel af kuldioxidet (CO_2) fra regenerationsbeholderen (10) ind i kuldioxid-elektrolysecellen (2).

12. Indretning (1) ifølge et af kravene 8 til 11, hvor den første katode (6) er en gasdiffusionselektrode.

13. Indretning (1) ifølge et af kravene 8 til 12, hvor gasvaskeindretningen (32) omfatter fyldlegemer eller en emballage.


1
36, PG
35, O_2
14, K1
20, A1, O_2
32
33
15, PG, CO_2
6
9
18, K, CO_2
8
2
7
3
19, A1
11, CO_2
5
4
12, K1
13, A1
16, CO_2
EL
EL
10