METHOD FOR ELECTROCHEMICAL REDUCTION OF CO2 IN AN ELECTROCHEMICAL CELL

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ABSTRACT
The invention refers to method for electrochemical reduction of CO2 in an electrochemical cell having a cathode and an anode. The method comprises: at the cathode, reducing the CO2; at the anode, oxidizing a first hydrocarbon generating a second hydrocarbon.

Diagram:
- CH4
- CO2
- C2H6
- C2H4
- 1
- 2
- 3
- 4
- 5
- 6
- 7
- 8
- 9
- 10
- 11
- 12
- 13
- 14
- 15
- 16
- 17
- 18
- 19

METHOD FOR ELECTROCHEMICAL REDUCTION OF CO2 IN AN ELECTROCHEMICAL CELL

TECHNICAL FIELD

[0001] The present invention relates to a method for electrochemical reduction of CO2 in an electrochemical cell.

BACKGROUND

[0002] Power plants for electric power generation produce large amounts of carbon dioxide by combustion of a fuel. Currently it is envisaged the need of a reduction of the carbon dioxide emission, because of the environmental impact of the carbon dioxide. In order to limit carbon dioxide emissions, power plants can be provided with separation plants which remove the carbon dioxide from the flue gas generated by the power plant; a gas with a low content of carbon dioxide is thus vented into the atmosphere while the carbon dioxide can be sequestered or used in another way.

[0003] In order to use the large amount of carbon dioxide collected by a separation plant associated to a power plant, US 2014/0151240 proposes to convert the carbon dioxide in a useful product in an electrochemical cell. In particular, US 2014/0151240 discloses to provide an absorber downstream of the power plant. At the absorber a capture solution captures the carbon dioxide and is then forwarded to the cathode of the electrolytic cell where the carbon dioxide is reduced to a hydrocarbon. According to US 2014/0151240 H2O is dissociated at the anode according to the equilibrium

\[ \text{H}_2\text{O} \leftrightarrow \text{O}_2 + 2\text{H}^+ + 2e^- \]

having a \( \Delta G = 4948.4 \text{ kJ/mol} \).

[0004] Since the \( \Delta G \) (i.e. variation of Gibbs energy) is positive, energy (in the form of electric energy) has to be supplied for the reaction to occur and since the value of \( \Delta G \) is high, the amount of energy to be supplied is high.

[0005] U.S. Pat. No. 8,444,844 proposes carbon dioxide reduction with an electrochemical cell in which at the anode an oxidation product can be made that can be subsequently used in producing another carbon compound. In particular, U.S. Pat. No. 8,444,844 teaches to supply, at the cathode, carbon dioxide together with a salt, such as bromide salt, and, at the anode, a reactant such as a halide salt.

[0006] According to U.S. Pat. No. 8,444,844 additional reagents are needed for the products discharged from the electrolytic cell to be converted into hydrocarbon. This implies plant complexity and costs.

[0007] US 2013/0140187 proposes carbon dioxide reduction with an electrochemical cell in which the cathode is supplied with carbon dioxide and the anode with an alcohol; at the cathode a first product such as CO, formic acid, formaldelyde, methanol, oxalate, etc. are collected, and at the anode a second product such as aldehyde, a ketone, carboxylic acid, etc. are collected.

SUMMARY

[0008] An aspect of the invention includes providing a method for electrochemical reduction of CO2 in an electrochemical cell and an electrochemical cell that requires limited electric energy supply when compared to the energy needed with H2O dissociation and, in addition, allow production of a hydrocarbon.

[0009] These and further aspects are attained by providing a method and an electrochemical cell in accordance with the accompanying claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] Further characteristics and advantages will be more apparent from the description of a preferred but non-exclusive embodiment of the method and electrochemical cell, illustrated by way of non-limiting example in the accompanying drawings, in which:

[0012] FIG. 1 shows an electrochemical cell in an embodiment of the invention.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0013] In the following the electrochemical cell is described first. The electrochemical cell can have the features of the electrochemical cell described in US 2014/0 151 240. The electrochemical cell 1 comprises a body 2 with a membrane 3 defining a cathode chamber 4 housing a cathode 5 and an anode chamber 6 housing an anode 7.

[0014] The cathode chamber 4 houses a catholyte 8 surrounding the cathode 5, and the anode chamber 6 houses an anolyte 9 surrounding the anode 7.

[0015] The cathode 5 and/or the anode 7 comprise an electro-conductive bar, for example comprising a metal bar or a bar with a metal coating; in addition the bar defining the cathode and/or anode can be a solid bar or a mesh bar.

[0016] The membrane 3 is an ion exchange membrane, i.e. a membrane that permits exchange of ions between the cathode and anode; for example the membrane can have the features described in US 2014/0 151 240.

[0017] The catholyte 8 and the anolyte 9 are preferably liquid catholyte and liquid anolyte and can be the same as those described in US 2014/0 151 240. Alternatively, the electrolytic cell can be a solid oxide electrolytic cell (with solid catholyte and anolyte) in which gaseous hydrocarbons are used for the reactions at the anode.

[0018] In addition, in order to improve contacting a water insoluble organic compound like the anolyte with the anode 7, a wetting agent such as anionic, cationic, non-ionic or ampholytic surfactants can be contained in the anolyte 9 and/or a hydrophobic coating like hydrocarbons or fluorinated hydrocarbons can be provided on the anode 7.

[0019] The electrochemical cell 1 also has an electric energy feeder 11. This feeder 11 is usually a DC electric energy feeder and can for example include a battery and/or rectifier connected to the electric grid and/or another device. The feeder 11 is connected between the cathode 5 and the anode 7; as known in the art, the cathode 5 is connected to the positive pole and the anode is connected to the negative pole of the feeder 11.

[0020] The electrochemical cell 1 preferably also has a circulating path 12 for circulating the catholyte outside of the cathode chamber 4 and a CO2 feeder 13 into the circulating path 12 for the catholyte.

[0021] Likewise, the electrochemical cell 1 also has a circulating path 15 for circulating the anolyte outside of the anode chamber 6 and a feeder 16 for supplying a first hydrocarbon into the circulating path 15 for the anolyte.
[0022] The electrochemical cell 1 further has outlets 18, 19 respectively at the cathode chamber 4 and at the anode chamber 6 for collecting products (typically gas products) generated during operation.

[0023] The operation of the electrochemical cell is apparent from that described and illustrated and is substantially the following.

[0024] Carbon dioxide is supplied via the CO₂ feeder 13 into the circulating path 12 and is supplied, together with the circulating catholyte into the cathode chamber 4. Catholyte circulation allows mixing of the catholyte and improving ion transport and the reactions at the cathode 5.

[0025] In addition, a first hydrocarbon is supplied into the circulating path 15; for example ethane C₂H₆ can be supplied into the circulating path 15. Other hydrocarbons can be used, such as for example propane C₃H₈, coal, lignite, coke, etc. In addition, instead of one hydrocarbon, also mixtures of hydrocarbons can be used; these mixtures can comprise any of ethane C₂H₆, propane C₃H₈, coal, lignite, coke, or other hydrocarbons. The hydrocarbon is mixed with the anolyte and hydrocarbon and anolyte are supplied together into the anode chamber 6. Anolyte circulation allows mixing of the anolyte and improving ion transport and the reactions at the anode 7.

[0026] Together with carbon dioxide supply into the cathode chamber 4 and hydrocarbon supply into the anode chamber 6, electric energy (typically DC energy) is supplied to the cathode 5 and anode 7 via the feeder 11.

[0027] Electric energy allows the following electrochemical reactions to take place:

at the cathode:

\[ 8\text{H}^+ + 2\text{e}^- + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \ \Delta G \approx -130.3 \text{ kJ/mole} \]

at the anode:

\[ 4\text{C}_2\text{H}_4 \leftrightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \ \Delta G = 271.3 \text{ kJ/mole} \]

with overall reaction being

\[ 4\text{C}_2\text{H}_4 + \text{CO}_2 \leftrightarrow 2\text{C}_2\text{H}_4 + 2\text{H}_2\text{O} + \text{CH}_4 \]

[0029] and gathering of methane CH₄ at the cathode 5 and ethylene C₂H₄ at the anode. Naturally even if according to the described example carbon dioxide CO₂ is reduced to methane CH₄, in different embodiments CO₂ can be reduced to CO, formic acid, methanol, ethanol, ethylene, propylene, etc. according to the particular reactions occurring. In addition, at the cathode 5 also water H₂O and/or some unreacted CO₂ can be collected; these products can be separated downstream of the outlet 18 in a separator. Likewise, at the anode 7 also water H₂O and/or some unreacted first hydrocarbon (e.g. C₂H₆) can be collected; these products can be separated downstream of the outlet 19 in a separator.

[0030] Advantageously, the electrochemical cell of the invention allows gathering of a useful product at the cathode and one or more hydrocarbons at the anode (the second hydrocarbon), while consuming carbon dioxide (at the cathode), with the need of limited electric energy input (because of the lower ΔG of the reaction at the anode) and with a substantially simple plant (because no additional reactors to complete the reactions and get the hydrocarbons or useful products are needed).

[0031] The present invention also refers to a method for electrochemical reduction of CO₂ in an electrochemical cell having a cathode and an anode. The method comprises

[0032] at the cathode, reducing the CO₂,

[0033] at the anode, oxidizing a first hydrocarbon generating a second hydrocarbon.

[0034] The first hydrocarbon comprises at least one among ethane (C₂H₆), propane (C₃H₈), coal, lignite, coke; in a preferred embodiment the first hydrocarbon is ethane (C₂H₆) and the second hydrocarbon is ethylene (C₂H₄). The first hydrocarbon can be in gas and/or liquid and/or solid form according to e.g. the pressure and temperature and can be a single compound or a mixture of different hydrocarbons.

[0035] The second hydrocarbon will depend on the first hydrocarbon and the oxidation reaction occurring at the anode 7.

[0036] Often, when the hydrocarbon is collected, it contains impurities; the method thus further comprises removing the second hydrocarbon from the anode and separating the second hydrocarbon from impurities that can for example comprise the first hydrocarbon.

[0037] Naturally the features described may be independently provided from one another.

1. A method for electrochemical reduction of CO₂ in an electrochemical cell having a cathode and an anode, the method comprising

   at the cathode, reducing the CO₂,
   at the anode, oxidizing a first hydrocarbon generating a second hydrocarbon.

2. The method of claim 1, wherein the first hydrocarbon comprises at least one among ethane (C₂H₆), propane (C₃H₈), coal, lignite, coke.

3. The method of claim 1, wherein the first hydrocarbon is ethane (C₂H₆) and the second hydrocarbon is ethylene (C₂H₄).

4. The method of claim 1, wherein the electrochemical cell comprises a body with a membrane defining a cathode chamber housing the cathode and an anode chamber housing the anode, the anode chamber housing a catholyte surrounding the cathode, the method further comprising circulating the catholyte outside of the cathode chamber.

5. The method of claim 4, wherein the catholyte is a liquid catholyte.

6. The method of claim 4, wherein the CO₂ is supplied into the catholyte circulating outside of the cathode chamber.

7. The method of claim 1, wherein the electrochemical cell comprises a body with a membrane defining a cathode chamber housing the cathode and an anode chamber housing the anode, the anode chamber housing an anolyte surrounding the anode, the method further comprising circulating the anolyte outside of the anode chamber.

8. The method of claim 7, wherein the anolyte is a liquid anolyte.

9. The method of claim 7, wherein the first hydrocarbon is supplied into the anolyte circulating outside of the anode chamber.

10. The method of claim 1, further comprising removing the second hydrocarbon from the anode and separating the second hydrocarbon from impurities.

11. The method of claim 10, wherein impurities comprise the first hydrocarbon.

12. The method of claim 1, wherein the anode is immersed in an anolyte containing a wetting agent and/or the anode has a hydrophobic coating.
13. An electrochemical cell for electrochemical reduction of CO₂, the electrochemical cell comprising
a cathode for reducing the CO₂,
an anode for oxidizing a first hydrocarbon generating a second hydrocarbon.

14. The electrochemical cell of claim 13, wherein the first hydrocarbon comprises at least one among ethane (C₂H₆), propane (C₃H₈), coal, lignite, coke.

15. The electrochemical cell of claim 13, further comprising a body with a membrane defining a cathode chamber housing the cathode and an anode chamber housing the anode, the cathode chamber housing a catholyte surrounding the cathode, the electrochemical cell further comprising a circulating path for the catholyte outside of the cathode chamber.

16. The electrochemical cell of claim 15, wherein the catholyte is a liquid catholyte.

17. The electrochemical cell of claim 15, further comprising a CO₂ feeder into the circulating path for the catholyte.

18. The electrochemical cell of claim 13, wherein the electrochemical cell comprises a body with a membrane defining a cathode chamber housing the cathode and an anode chamber housing the anode, the anode chamber housing an anolyte surrounding the anode, the electrochemical cell further comprising a circulating path for the anolyte outside of the anode chamber.

19. The electrochemical cell of claim 18, wherein the anolyte is a liquid anolyte.

20. The electrochemical cell of claim 18, further comprising a feeder for the first hydrocarbon into the circulating path for the anolyte.

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