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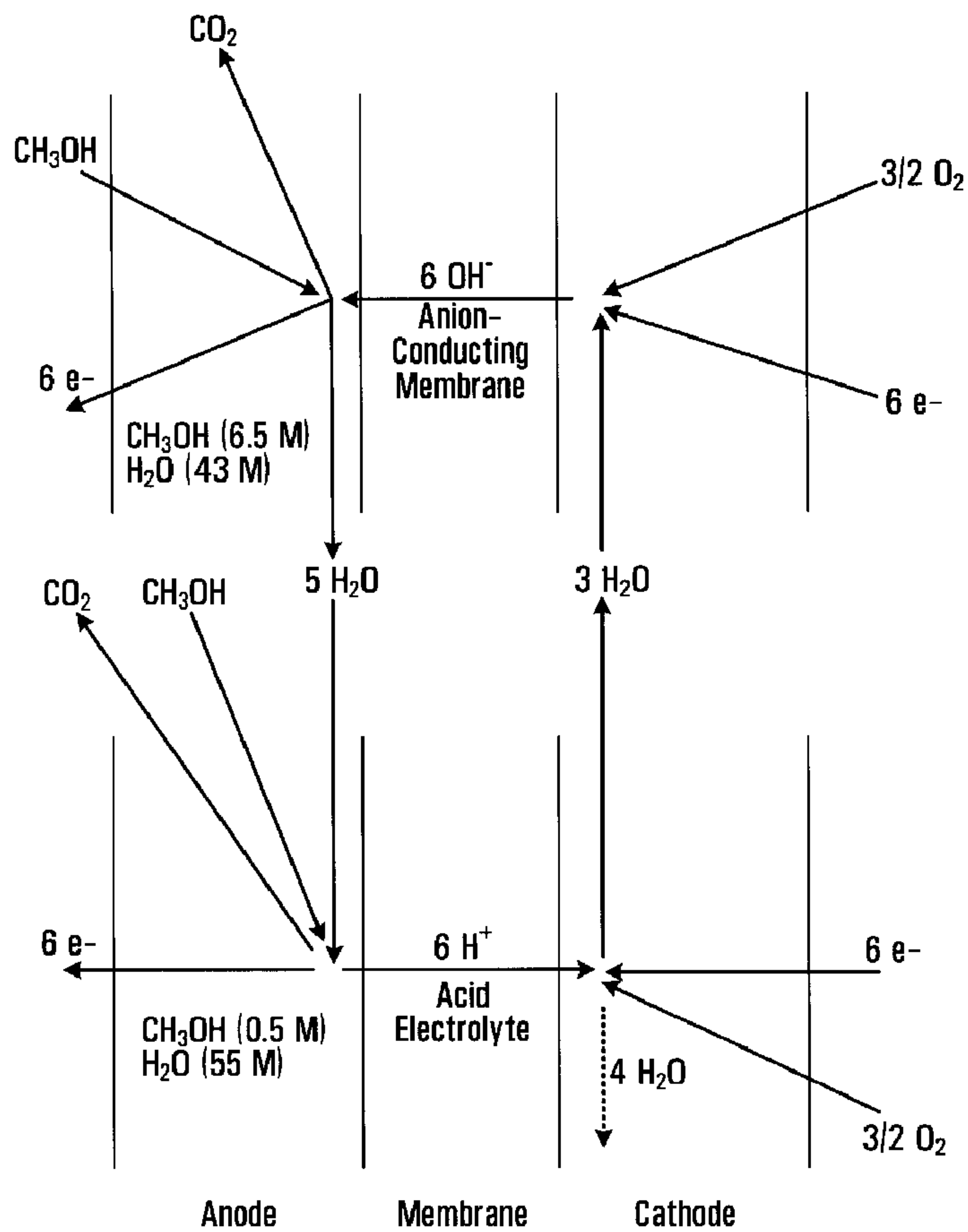
(54) **Titre :** PILE A COMBUSTIBLE ALCALINE A OXYDATION DIRECTE DU METHANOL
(54) **Title:** ALKALINE DIRECT METHANOL FUEL CELL



(57) **Abrégé/Abstract:**
The invention relates to a fuel cell, in particular a methanol fuel cell which has an anion-conductive membrane. The protons required for the formation of hydroxyl ions are supplied to the cathode chamber in the form of water. The water resulting from the

(57) Abrégé(suite)/Abstract(continued):
reaction is produced at the anode. The method requires the use of alkaline media both in the anode chamber and in the cathode chamber.

Abstract

The invention relates to a fuel cell, in particular a methanol fuel cell which has an anion-conductive membrane. The protons required for the formation of hydroxyl ions are supplied to the cathode chamber in the form of water. The water resulting from the reaction is produced at the anode. The method requires the use of alkaline media both in the anode chamber and in the cathode chamber.

TRANSLATION

DESCRIPTION

ALKALINE DIRECT METHANOL FUEL CELL

The invention relates to a fuel cell, especially a methanol fuel cell, as well as to a method of operating this fuel cell.

A fuel cell has a cathode, an electrolyte as well as an anode. The cathode is supplied with an oxidation medium, for example, air or oxygen and the anode is supplied with a fuel, for example, hydrogen or methanol.

Various fuel cell types are known including for example the SOFC fuel cell (SOFC = Solid oxide fuel cell) from the publication DE 44 30 958 C1 as well as the PEM fuel cell (PEM = Proton exchange membrane) from the publication DE 195 31 852 C1.

The operating temperature of a PEM fuel cell is about 80° C. A PEM fuel cell can in principle be either acidic or alkaline depending upon the type of membrane or the working medium. Usually protons form at the anode of a PEM fuel cell with a proton conductor in the presence of the fuel by means of a catalyst. The protons traverse the electrolyte and combine at the cathode side with oxygen stemming from the oxidation medium to water. Electrons are thereby liberated and electrical energy is generated. The drawback of a methanol fuel cell with a proton conductor is that the protons under the influence of the electric field also carry water molecules with them in their solvate shells. This electrophoresis effect is associated with a very high drag factor (number of entrained water molecules per proton). This means on the one hand that too much water is transported from the anode to the cathode which is disadvantageous for the thermal balance and on the other hand that methanol is also entrained so that there is a significant reduction in efficiency because of the formation in general of a mixed potential at the cathode.

Multiple fuel cells are electrically and mechanically connected together by connecting elements as a rule in order to produce greater electrical powers. These arrangements are known as fuel cell stacks.

As fuels, among others, methane or methanol can be used. The mentioned fuels are transformed by reformation or oxidation among others to hydrogen or hydrogen-rich gases.

There are two types of methanol fuel cells. The so-called indirect methanol fuel cells in which initially in a preliminary process step a hydrogen-rich gas mixture is produced and which is introduced into a polymer electrolyte fuel cell of the usual hydrogen type with anodic Pt/Ru-catalyst. This process variant is carried out in two stages: the gas production and the usual fuel cell.

A further significantly simpler variant which is significant from the process technology point of view is the so-called direct methanol fuel cell (DMFC) in which the methanol without intervening stages in the process technology is directly fed to the fuel cell. This cell has by comparison to the first, however, the drawback that the direct electrochemical methanol oxidation is kinetically a strongly limited process, which, in comparison to a hydrogen fuel cell is signified by greater losses in cell voltage. Even the best results of the DMFC cell at this time makes it hardly likely that these cells can compete in classical constructions with the indirect methanol fuel cells.

In this connection it may be noted that both the methanol permeation rate and the water vaporization enthalpy are too high in the cathode compartment of such cells. Furthermore, because of the unsatisfactory methanol oxidation rate it is necessary to maintain the operating temperature of the cell significantly above 100°C. There is, however, no appropriate electrolyte which can be function at temperatures above 120°C.

To be economical by comparison with the indirect methanol cell, the DMFC must have by comparison to the indirect cell at the same current density only about 100 mV smaller voltage (with MeOH permeation) or a voltage about 150mV smaller without permeation. As simulation results have shown, the greater loses have their origins in anodic voltage resulting from the highly irreversible electrode kinetics. Consequently, even the catalytic coatings must be uneconomically high; because of the methanol permeation, the cathodic catalyst coating should be ten times higher than that which is the case in the hydrogen cell.

An object of the invention is to provide a fuel cell, especially a fuel cell stack, especially for the conversion of methanol which is effective and can avoid the aforementioned drawbacks. Further it is an object of the invention to provide a method of operating a cell.

According to one aspect of the present invention, there is provided a fuel cell system comprising: a first methanol fuel cell comprising a first anode compartment, wherein the first anode compartment comprises an anode; a first cathode compartment comprising a cathode; an anion-conducting membrane between said first anode compartment and said first cathode compartment; and a water pathway between said first anode compartment and said first cathode compartment for removing water formed at said anode and delivering water to said first cathode compartment; wherein said water pathway comprises a second methanol fuel cell comprising an acid electrolyte connected to said first methanol fuel cell, wherein said second methanol fuel cell comprises a second anode compartment receiving water formed in the first anode compartment and a second cathode compartment for delivering water to the first cathode compartment of the first methanol fuel cell.

According to another aspect of the present invention, there is provided the fuel cell system described herein, wherein the water pathway comprises a means for recovering methanol therefrom.

According to still another aspect of the present invention, there is provided the fuel cell system described herein, wherein the means for recovering methanol comprises the acid electrolyte of the second methanol fuel cell.

According to yet another aspect of the present invention, there is provided a fuel cell stack comprising the fuel cell system as described herein and at least one further methanol fuel cell comprising an acid electrolyte.

According to a further aspect of the present invention, there is provided a method of operating the fuel cell system described herein, comprising the steps of: (a) passing hydroxyl ions from the first cathode compartment to the first anode compartment through the anion-conducting membrane; (b) feeding a mixture comprising methanol and water from the first anode compartment to the second anode compartment; and (c) feeding water formed in the second cathode compartment to the first cathode compartment.

According to yet a further aspect of the present invention, there is provided a method of operating the fuel cell stack described herein, wherein the fuel cell system is operated according to the method described herein, and methanol generated from operation of the fuel cell system is supplied to a methanol fuel cell of the at least one further methanol fuel cell comprising an acid electrolyte.

The methanol fuel cells within the scope of the claims encompass an anode compartment with an anode and a cathode compartment with a cathode as well as a membrane between the anode and a cathode which is anion conducting. An anion-conducting membrane is permeable to anions as, for example, hydroxide ions. A suitable membrane is for example a membrane having a basis of anion-conducting polymer electrolytes. In addition, the methanol fuel cells according to the claims encompass a means for conducting water out of the anode compartment to the cathode compartment. The means according to the invention for conducting water is thus not exclusively limited to water. This means can conduct also other liquids together with water; especially, this means can conduct a methanol/water mixture from the anode compartment to the cathode compartment of a fuel cell.

In an advantageous configuration of the fuel cell in accordance with the invention, the means for conducting water out of the anode compartment into the cathode compartment encompass a further fuel cell with an acid electrolyte which is suitable for separation of methanol.

Advantageously the fuel cell stack according to the invention has at least two methanol fuel cells with an anion-conducting membrane and a further fuel cell with an acid electrolyte.

With this fuel cell stack methanol can be advantageously converted into electrical energy especially effectively and indeed in a process variant which is based on the use of an anion conducting polymer electrolyte.

The invention comprehends the use of an anion-conducting membrane which is permeable to the hydroxyl ions. It will be understood that the ions entrain no water or only a small amount of water so that the protons which serve for hydroxyl-ion formation must be supplied as water to the cathode whereby the product water is formed anodically. The use of an anion conductor shifts the chemistry of this process by contrast to that of the conventional DMFC and both as to the methanol oxidation and the oxygen reduction electrochemistry in an alkali media. This has however the following significant advantages:

. The anodic methanol oxidation is carried out by means of a basic catalyzed dehydrogenation whereby the hydrogen formed is itself electrochemically active. It is thus to be expected that the overall catalyst will be more effective than in acidic medium.

. The cathodic oxygen reduction in an alkali medium is not as strongly blocked as in an acid. Here as well a voltage recovery can be expected.

. It is possible to eliminate the need for noble metals as catalysts. Raney nickel can be used as the electrode material for the methanol electrode in alkali medium. As for the oxygen electrode, for example, Ag, Co or Ni are conceivable as catalysts.

In an alkaline fuel cell water is consumed for the formation of OH^--ions at the cathode side. At the anode side water arises which must be removed from the cycle. Since a limiting current is hardly conceivable with complete conversion of the methanol used, there is always methanol present in the anodic residue which is not permissible. The non-recyclable water must thus be cleaned as an exhaust gas, i.e. must be freed from methanol which can be achieved for example by evaporation. However, the evaporation requires such an amount of energy that the entire process can be uneconomical.

In the context of the invention, a cascade purification scheme is proposed as is described below.

The process diagram has been shown in FIG. 1. It is based upon the following reaction equations:

Anode: $CH_3OH + 6\ OH^- \rightarrow CO_2 + 5\ H_2O + 6e^-$

Cathode: $3/2\ O_2 + 3\ H_2O + 6e^- \rightarrow 6\ OH^-$

The product water is enriched in the anode circulation from which it must be removed. For that purpose a stack cascade scheme is proposed which is comprised of two parts: alkaline cells which reduce the concentration of the supplied methanol with a high energy yield from a high concentration (in FIG. 1 as an example 6.5 M MeOH is assumed) to a concentration of 0.5 M. At these concentrations, at the end of the cascade a conventional proton conducting DMFC cell is connected from which the product water is removed with a lower energy output and with a higher drag coefficient, from the anode circulation. A part of the product water is fed to the cathode compartment of the alkali cells for hydroxyl ion formation. In FIG. 1 as an example the following are assumed:

MeOH- concentration at cascade inlet: 6.5 M.

H_2O concentration at cascade inlet: 43 M.

MeOH- depletion: down to 0.5 M, corresponding to an H_2O enrichment to 55 M.

Drag factor at the protonic cells at 90°C: 4.0.

The drag factor of 4.0 corresponds to the following DMFC cell reaction:

Anode: $CH_3OH + H_2O + 24\ H_2O \rightarrow CO_2 + 6\ [H(H_2O)_4]^+ + 6e^-$

Cathode: $6\ [H(H_2O)_4]^+ + 3/2\ O_2 + 6e^- \rightarrow 3\ H_2O + 24\ H_2O$

Water Discharge: $24\ H_2O$ (Anode) $\rightarrow$ $24\ H_2O$ (cathode)

From the above equations, there is a total of twenty-four moles of H_2O discharged from the anode compartment per mole of CH_3OH and 2 moles of H_2O per mole of CH_3 are electrochemically formed. For the electrochemical balance 2 moles of H_2O suffice, i.e. 24 moles of H_2O correspond to the mass balance of the alkali cell. With these relationships the alkali cells utilize 92% of the MeOH introduced (with high energy yield) while 8% is used in the proton conducting cells. The stoichiometric water balance corresponds to:

Anode: $5\ H_2O + CH_3OH \rightarrow CO_2 + 6\ H^+ + 6\ e^- + 4\ H_2O$

Cathode: $3/2\ O_2 + 6\ H^+ + 6\ e^- + 4\ H_2O \rightarrow 7\ H_2O$

The reaction scheme satisfies the overall reaction equation for the combustion of methanol

$$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2\ H_2O$$

Which thus characterizes a DMFC reaction process.

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CLAIMS:

1. A fuel cell system comprising:

a first methanol fuel cell comprising a first anode compartment, wherein the first anode compartment comprises an anode;

a first cathode compartment comprising a cathode;

an anion-conducting membrane between said first anode compartment and said first cathode compartment; and

a water pathway between said first anode compartment and said first cathode compartment for removing water formed at said anode and delivering water to said first cathode compartment;

wherein said water pathway comprises a second methanol fuel cell comprising an acid electrolyte connected to said first methanol fuel cell, wherein said second methanol fuel cell comprises a second anode compartment receiving water formed in the first anode compartment and a second cathode compartment for delivering water to the first cathode compartment of the first methanol fuel cell.

2. The fuel cell system of claim 1, wherein the water pathway comprises a means for recovering methanol therefrom.

3. The fuel cell system of claim 2, wherein the means for recovering methanol comprises the acid electrolyte of the second methanol fuel cell.

4. A fuel cell stack comprising the fuel cell system as defined in any one of claims 1 to 3 and at least one further methanol fuel cell comprising an acid electrolyte.

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5. A method of operating the fuel cell system defined in any one of claims 1 to 3, comprising the steps of:

(a) passing hydroxyl ions from the first cathode compartment to the first anode compartment through the anion-conducting membrane;

(b) feeding a mixture comprising methanol and water from the first anode compartment to the second anode compartment; and

(c) feeding water formed in the second cathode compartment to the first cathode compartment.

6. A method of operating the fuel cell stack defined in claim 4, wherein the fuel cell system is operated according to the method defined in claim 5, and methanol generated from operation of the fuel cell system is supplied to a methanol fuel cell of the at least one further methanol fuel cell comprising an acid electrolyte.

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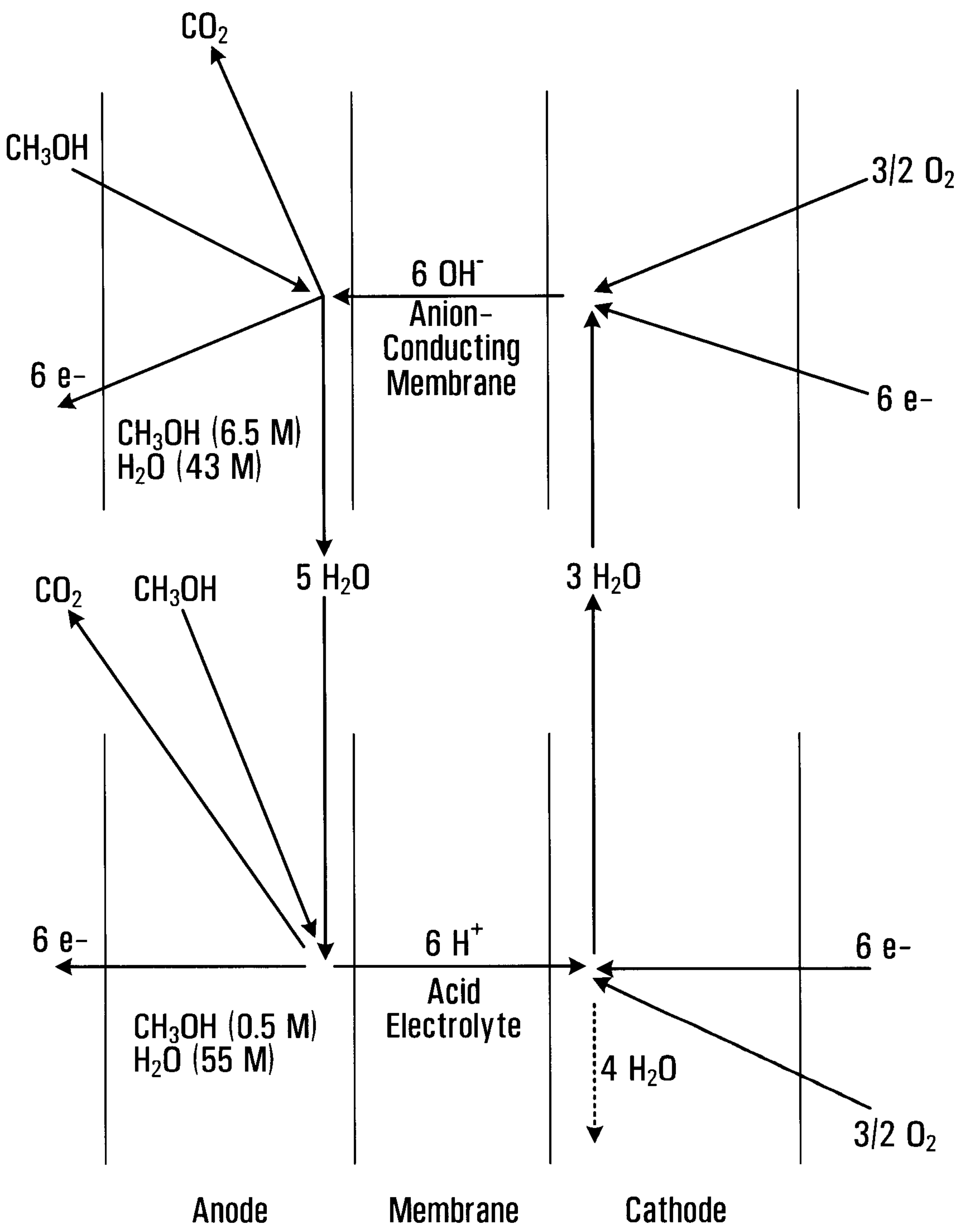
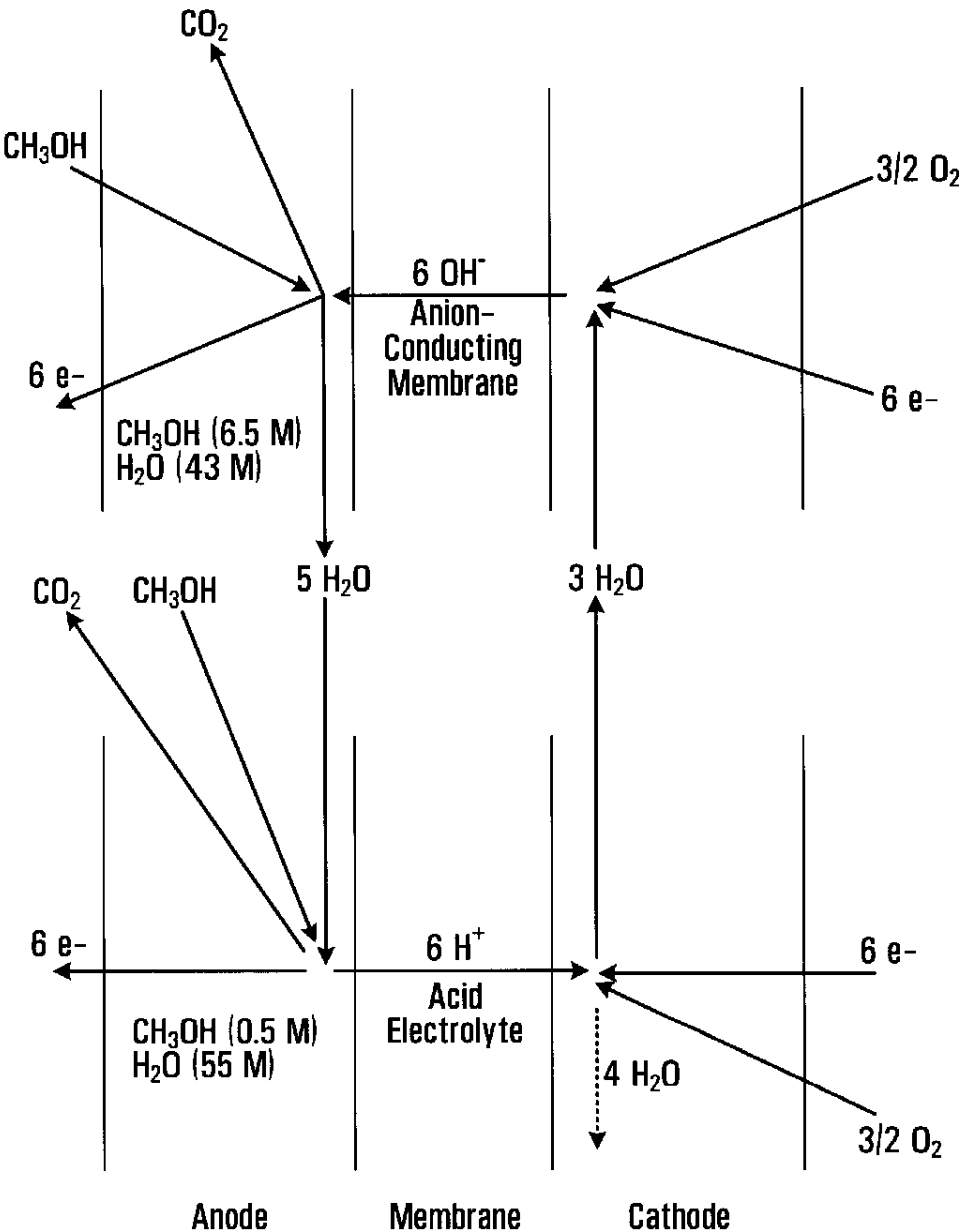
PATENT AGENTS



CO_2
CH_3OH
$3/2\ O_2$
$6\ OH^-$
Anion-
Conducting
Membrane
6 e-
6 e-
CH_3OH (6.5 M)
H_2O (43 M)
$5\ H_2O$
$3\ H_2O$
CO_2
CH_3OH
6 e-
$6\ H^+$
6 e-
Acid
Electrolyte
CH_3OH (0.5 M)
H_2O (55 M)
$4\ H_2O$
$3/2\ O_2$
Anode
Membrane
Cathode

FIG. 1



CO_2
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Anion-
Conducting
Membrane
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CH_3OH (6.5 M)
H_2O (43 M)
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3 H_2O
CO_2
CH_3OH
6 e−
6 H^+
6 e−
Acid
Electrolyte
CH_3OH (0.5 M)
H_2O (55 M)
4 H_2O
$3/2\ O_2$
Anode
Membrane
Cathode