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(54) Title: FUEL CELLS

(57) Abstract: The invention provides a fuel cell comprising an anode in an anode region of the cell and a cathode in a cathode
region of the cell, the anode being separated from the cathode by an ion selective polymer electrolyte membrane, the anode region
of the cell being supplied in use thereof with an alcoholic fuel, the cathode region of the cell being supplied in use thereof with an
oxidant, the cell being provided with means for generating an electrical circuit between the anode and the cathode and with a non-
volatile redox couple in solution in flowing fluid communication with the cathode in the cathode region of the cell, the redox couple
being at least partially reduced at the cathode in operation of the cell, and at least partially re-generated by reaction with the oxidant
after such reduction at the cathode, the redox couple and/or the concentration of the redox couple in the catholyte solution being
selected so that the current density generated by the cell in operation is substantially unaffected by the crossover of the alcoholic fuel
from the anode region of the cell to the cathode region of the cell across the polymer electrolyte membrane.

FUEL CELLS

The present invention relates to fuel cells, in particular to fuel cells in operation of which an alcohol is supplied as fuel to the anode region of the

5   cell.   Such cells have applications in microfuel cells for electronic and portable electronic components, and also in larger fuel cells for the automotive industry.

A fuel cell is an electrochemical energy conversion device that converts

10   fuel and oxidant into reaction products, producing electricity and heat in the process. In one example of such a cell, methanol is used as fuel, and air or oxygen as oxidant, and the products of the reaction are carbon dioxide and water. The electrochemical reactions in this cell in operation may be summarised as follows:

15

Anode $CH_3OH + H_2O$ $\leftrightharpoons$ $CO_2 + 6H^+ + 6e^-$

Cathode $^3/_2O_2 + 6H^+ + 6e^-$ $\leftrightharpoons$ $3H_2O$

Overall $CH_3OH + ^3/_2O_2$ $\leftrightharpoons$ $CO_2 + 2H_2O$
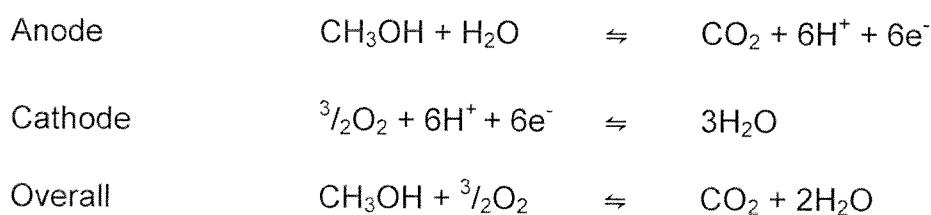
20   The methanol fuel and oxidant are fed respectively into catalysing, diffusion-type electrodes separated by an electrolytic membrane which allows the passage of protons from the anode chamber to the cathode chamber to balance the cathode reaction. The electrons generated in the

anode chamber flow in an external electrical circuit and are returned to the cathode having provided the power output from the cell. Such fuel cells are known as direct methanol fuel cells (DMFCs). Various types of membrane may be used, such as polymer electrolyte membranes

5   (PEMs), comprising for example Nafion™. Fuel cells based on polymer electrolyte membranes (PEM fuel cells) are convenient for portable applications such as portable electronics and automotive technology due to their relatively low temperatures of operation. Further or alternative adaptations to the PEM barrier include the provision of a bimembrane as

10 described in our co-pending application PCT/EP2006/060640.

WO-A-2006/012637 discloses a reactor and corresponding method for producing electrical energy using a fuel cell by selectively oxidising CO at room temperature using polyoxometallate compounds.

US-A-2005/0112055 discloses a catalyst comprising di-ruthenium-

15 substituted polyoxometallate and a method of using the electrocatalyst to generate oxygen.

US-A-2004/0137297 discloses an ion exchange membrane said to be useful for the diaphragm of a direct methanol type fuel cell.

Methanol and other low molecular weight alcohols are convenient fuels

20 for portable fuel cells because their energy density is relatively high, eg, for methanol, six moles of electrons being generated in the electrochemical half cell for every mole of fuel consumed. However,

DMFCs typically suffer from crossover effects – methanol is transported across the membrane by diffusion and electro-osmosis. This causes a reduction in the performance of the fuel cell by the effect of methanol being oxidized at the cathode, typically comprising Pt or other noble metal

5   catalyst. Here the methanol is oxidized at the potentials of oxygen reduction. The potential and current are reduced, causing a loss in power density; the open circuit potential is also reduced.

Conventionally, routes to reduce the methanol crossover effect have

10   included:

i)   Increasing the membrane thickness – typically 170µm Nafion is used instead of the more common 50µm membrane for hydrogen fuel cells. This increases the resistance of the membrane – whilst not completely eliminating the crossover

15   impact.

ii)   Using an alternative membrane to the Nafion-type sulphonated fluoropolymer. Usually these membranes require higher temperatures (>100° C) to operate effectively, or conduct less

        well or swell.

20   iii)   Using selective catalysts for the cathode. These are generally poorer catalysts for oxygen reduction than noble metal-containing catalysts such as Pt and Pt-containing catalysts.

The phenomenon of methanol crossover and potential solutions have been reviewed recently:

- International activities in DMFC R&D: status of technologies and potential applications, R Dillon, S Sriinivasan, A S Arico, V Antonucci, J Power Sources, 127, 112 (2004).
- M P Hogarth, T R Ralph, Platinum Metal Reviews, 46, 146 (2002).
- A Heinzel, V M Barragan, J Power Sources, 84,70 (1999).

It is an object of the present invention to provide an improved alcohol-fuelled fuel cell. In particular, it is intended overcome or ameliorate one or more of the aforesaid disadvantages caused by crossover of the alcoholic fuel across the membrane separating the anode from the cathode. It is a more specific object of the invention to reduce the impact of crossover of direct methanol or other alcohol fuel cells whilst being able to operate at a temperature below that requiring applied pressure, and without unsatisfactorily compromising cell performance.

According to the present invention there is provided a fuel cell comprising an anode in an anode region of the cell and a cathode in a cathode region of the cell, the anode being separated from the cathode by an ion selective polymer electrolyte membrane, the anode region of the cell being supplied in use thereof with an alcoholic fuel, the cathode region of the cell being supplied in use thereof with an oxidant, the cell being provided with means

for generating an electrical circuit between the anode and the cathode and with a non-volatile redox couple in solution in flowing fluid communication with the cathode in the cathode region of the cell, the redox couple being at least partially reduced at the cathode in operation of the cell, and at least partially re-generated by reaction with the oxidant after such reduction at the cathode, the redox couple and/or the concentration of the redox couple in the catholyte solution being selected so that the current density for a given potential generated by the cell in operation is substantially unaffected by the oxidation of alcoholic fuel due to crossover from the anode region of the cell to the cathode region of the cell across the polymer electrolyte membrane.

By "substantially unaffected" is preferably meant that the current density, for any given potential, of alcoholic fuel oxidation at the cathode when the cell in operation at a particular temperature is less than about 10%, more preferably less than about 5%, most preferably by less than about 1% over a period of time during which crossover of fuel across the polymer electrolyte membrane occurs.

A fuel cell in accordance with the invention may conveniently be tested for compliance with these and the following criteria by test doping the cathode region of the cell with the alcoholic fuel, for example at a concentration of alcoholic fuel in the doped catholyte solution comparable to that found due to crossover of fuel from the anode.

A fuel cell is provided in accordance with the invention in which the current density for any given potential due to oxidation of the alcoholic fuel is less than about 10%, more preferably less than about 5% and mostre

5   preferably less than about 1% when the cathode chamber is supplied with alcoholic fuel at a concentration comparable to that created by crossover.

The invention therefore provides a cathode regenerative redox flow system comprising a liquid flowing catholyte solution and a chamber for

10   the regeneration of a redox species consumed at the electrode by oxygen. Surprisingly this has been found to reduce the impact of alcohol fuel, eg methanol, crossover. Without wishing to be limited by theory, it appears that methanol is effectively inactive at the cathode, enabling the catholyte redox species to be unimpeded in its reduction at the cathode.

15

In operation the fuel cell will usually provide electromotive force to some external mechanism (the drive shaft of an automobile or the processor of an electronic component, for example).

20   Suitable fuels include low molecular weight alcohols such as methanol, ethanol, propanol, isopropanol and butanol, dipropylene glycol and ethylene glycol.

Suitable oxidant gas materials include oxygen and air and hydrogen peroxide.

Preferably the anode electrode comprises a diffusion layer and an electrocatalyst layer. The diffusion layer is suitably of a graphitic nature, and the electrocatalyst layer is suitably of finely divided platinum or palladium. Platinum based alloys are also suitable for use in one or both electrodes, the alloy metal being suitably selected from tin, iridium, osmium, rhenium or ruthenium. Generally speaking, the choice of alloy depends on the fuel to be oxidised at the anode electrode. Platinum-ruthenium alloy anodes are preferable for electro-oxidation of methanol, for example.

The cathode in the redox fuel cell of the invention may comprise as cathodic material carbon, platinum, nickel, metal oxide species. However, it is preferable that expensive cathodic materials are avoided, and therefore preferred cathodic materials include carbon, nickel, metal oxide. The cathodic material may be constructed from a fine dispersion of particulate cathodic material, the particulate dispersion being held together by a suitable adhesive, or simply by the proton conducting polymeric material. The cathode is designed to create maximum flow of redox mediator to the cathode surface. Thus it may consist of shaped flow regulators or a three dimensional electrode; the liquid flow may be managed in a flow-by arrangement where there is a liquid channel

adjacent to the electrode, or in the case of the three dimensional electrode, where the liquid is forced to flow through the electrode. It is intended that the surface of the electrode is also the electrocatalyst, but it may be beneficial to adhere the electrocatalyst in the form of deposited particles on the surface of the electrode.

Transition metal ions, and complexes of transition metal ions form suitable redox couples for use in the fuel cell of the invention. Suitable transition metals include vanadium, molybdenum, iron, manganese and copper. One example of a suitable redox couple is the ferrous/ferric phenanthroline complex. Other examples include polyoxometallates. In one fuel cell of the invention, the redox couple comprises a polyoxometallate species. In this case the catholyte solution preferably comprises at least about 0.1M of a polyoxometallate.

The polyoxometallate when used as the redox species may be represented by the formula:

$$X_a[Z_bM_cO_d]$$
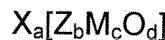
wherein:

X is selected from hydrogen, alkali metals, alkaline earth metals, ammonium and combinations of two or more thereof;

Z is selected from B, P, S, As, Si, Ge, Ni, Rh, Sn, Al, Cu, I, Br, F, Fe, Co,

Cr, Zn, H_2, Te, Mn and Se and combinations of two or more thereof;

M is a metal selected from Mo, W, V, Nb, Ta, Mn, Fe, Co, Cr, Ni, Zn Rh,

Ru, Tl, Al, Ga, In and other metals selected from the $1^{st}, 2^{nd}$ and 3rd

transition metal series and the lanthanide series, and combinations of two

or more thereof;

a is a number of X necessary to charge balance the $[M_cO_d]$ anion;

b is from 0 to 20, more preferably 0-2 ;

c is from 1 to 40; and

d is from 1 to 180.

Vanadium and molybdenum, and combinations thereof, are particularly

preferred for M.

Phosphorus is particularly preferred for Z.

A combination of hydrogen and an alkali metal and/or alkaline earth metal

is particularly preferred for X.   One such preferred combination is

hydrogen and sodium.

Specific examples of polyoxometallates include molybdophosphoric acid,

$H_3PMo_{12}O_{40}$ and molybdovanadophosphosphoric acid, $H_5PMo_{10}V_2O_{40}$.

Thus, according to a first aspect of the present invention, there is provided a fuel cell in accordance with the invention wherein the catholyte solution comprises a polyoxometallate catalyst. In a preferred embodiment of the present invention, the catalyst comprises vanadium. In a more preferred

5   embodiment, the catalyst comprises vanadium and molybdenum. In a preferred embodiment of the present invention, the polyoxometallate comprises vanadium, more preferably vanadium and molybdenum. Thus, the catalyst may be $H_3Na_2PMo_{10}V_2O_{40}$. Alternatively, the catalyst may be $H_3Na_3PMo_9V_3O_{40}$ or $H_3Na_4PMo_8V_4O_{40}$ and compounds of intermediate

10 composition. In addition, a mixture of these or other polyoxometallate catalysts is also envisaged. For this embodiment, preferably, at least one X is hydrogen. However, it is also preferred that not all X be hydrogen. More preferably, at least two of X are not hydrogen. X comprising at least one hydrogen and at least one other material selected from alkali metals,

15 alkaline earth metals, ammonium and combinations of two or more thereof is preferred.

The concentration of the polyoxometallate in the catholyte solution is preferably at least about 0.1M, preferably at least about 0.15M, more

20 preferably at least about 0.175M and most preferably at least about 0.2M.

Accordingly, the present invention provides a redox fuel cell comprising an anode and a cathode separated by an ion selective polymer electrolyte membrane; means for supplying an alcoholic fuel to the anode region of

the cell; means for supplying an oxidant to the cathode region of the cell; means for providing an electrical circuit between the anode and the cathode; a solution containing non-volatile catholyte components flowing in fluid communication with the cathode, the catholyte solution comprising

5   a redox couple being at least partially reduced at the cathode in operation of the cell, and at least partially re-generated by reaction with the oxidant after such reduction at the cathode, the catholyte solution comprising at least about 0.1M of the said redox couple.

10   In one preferred embodiment of the invention, the ion selective PEM is a cation selective membrane which is selective in favour of protons versus other cations.

The cation selective polymer electrolyte membrane may be formed from

15   any suitable material, but preferably comprises a polymeric substrate having cation exchange capability. Suitable examples include fluororesin-type ion exchange resins and non-fluororesin-type ion exchange resins. Fluororesin-type ion exchange resins include perfluorocarboxylic acid resins, perfluorosulfonic acid resins, and the like. Perfluorocarboxylic acid

20   resins are preferred, for example "Nafion" (Du Pont Inc.), "Flemion" (Asahi Gas Ltd),"Aciplex" (Asahi Kasei Inc), and the like. Non-fluororesin-type ion exchange resins include polyvinylalcohols, polyalkylene oxides, styrene-divinylbenzene ion exchange resins, and the like, and metal salts thereof. Preferred non-fluororesin-type ion exchange resins include polyalkylene

oxide-alkali metal salt complexes. These are obtainable by polymerizing an ethylene oxide oligomer in the presence of lithium chlorate or another alkali metal salt, for example. Other examples include phenolsulphonic acid, polystyrene sulphonic, polytriflurostyrene sulphonic, sulphonated trifluorostyrene, sulphonated copolymers based on α,β,β-triflurostyrene monomer, radiation-grafted membranes. Non-fluorinated membranes include sulphonated poly(phenylquinoxalines), poly (2,6 diphenyl-4-phenylene oxide), poly(arylether sulphone), poly(2,6-diphenylenol); acid-doped polybenzimidazole, sulphonated polyimides; styrene/ethylene-butadiene/styrene triblock copolymers; partially sulphonated polyarylene ether sulphone; partially sulphonated polyether ether ketone (PEEK); and polybenzyl suphonic acid siloxane (PBSS).

In some cases it may be desirable for the ion selective polymer electrolyte membrane to comprise a bi-membrane. The bimembrane if present will generally comprise a first cation selective membrane and a second anion selective membrane. In this case the bimembrane may comprise an adjacent pairing of oppositely charge selective membranes. For example the bi-membrane may comprise at least two discreet membranes which may be placed side-by-side with an optional gap therebetween. Preferably the size of the gap, if any, is kept to a minimum in the redox cell of the invention. The use of a bi-membrane may be used in the redox fuel cell of the invention to maximise the potential of the cell, by maintaining the potential due to a pH drop between the anode and catholyte solution.

Without being limited by theory, in order for this potential to be maintained in the membrane system, at some point in the system, protons must be the dominant charge transfer vehicle. A single cation-selective membrane may not achieve this to the same extent due to the free movement of other

5   cations from the catholyte solution In the membrane.

In this case the cation selective membrane may be positioned on the cathode side of the bimembrane and the anion selective membrane may be positioned on the anode side of the bimembrane. In this case, the

10   cation selective membrane is adapted to allow protons to pass through the membrane from the anode side to the cathode side thereof in operation of the cell. The anion selective membrane is adapted substantially to prevent cationic materials from passing therethrough from the cathode side to the anode side thereof, although in this case anionic materials may

15   pass from the cathode side of the anionic-selective membrane to the anode side thereof, whereupon they may combine with protons passing through the membrane in the opposite direction. Preferably the anion selective membrane is selective for hydroxyl ions, and combination with protons therefore yields water as product.

20

In a second embodiment of the invention the cation selective membrane is positioned on the anode side of the bimembrane and the anion selective membrane is positioned on the cathode side of the bi-membrane. In this case, the cation selective membrane is adapted to allow protons to pass

through the membrane from the anode side to the cathode side thereof in operation of the cell. In this case, anions can pass from the cathode side into the interstitial space of the bimembrane, and protons will pass from the anode side. It may be desirable in this case to provide means for

5   flushing such protons and anionic materials from the interstitial space of the bimembrane. Such means may comprises one or more perforations in the cation selective membrane, allowing such flushing directly through the membrane. Alternatively means may be provided for channelling flushed materials around the cation selective membrane from the interstitial space

10   to the cathode side of the said membrane.

According to another aspect of the present invention, there is provided a method of operating a proton exchange membrane fuel cell comprising the steps of:

15   a)   forming H^+ ions by the oxidation of an alcoholic fuel at an anode situated adjacent to a proton exchange membrane;

b)   supplying a catholyte comprising a non-volatile redox couple solution in an oxidised state to a cathode situated oppositely adjacent to the proton exchange membrane; and

20   c)   allowing the redox couple to become reduced upon contact with the cathode concomitantly with H^+ ions passing through the membrane to balance charge.

In a preferred embodiment, the catholyte is supplied from a catholyte reservoir.

The method of the above fourth aspect may additionally comprise the step

5   of:

d)   passing the catholyte from the cathode to a reoxidation zone wherein the catalyst is reoxidised.

In this embodiment, the cell is cyclic and the redox couple in the cathode

10   can be repeatedly oxidised and reduced without having to be replaced.

The invention will now be more particularly described with reference to the following Figures and Examples, in which:

15   FIG. 1a shows the I-V curves of a fuel cell in accordance with the invention and described in Example 1 using POM (7 ml/min ~0.9 M vanadium (V) in ~0.3 M POM) in the cathode, 2 ml/min 1.0 M methanol in the anode.

FIG. 1b shows the power densities of a fuel cell in accordance with the

20   invention and described in Example 1 using POM (7 ml/min ~0.9 M vanadium (V) in ~0.3 M POM) in the cathode, 2 ml/min 1.0 M methanol in the anode.

FIG 2 shows a comparison of conventional DMFC with a POM/DMFC system (70 ml/min ~0.3 M POM solution, 2 ml/min 1.0 M methanol, membrane: Nafion 115, anode: PtRu, cathode: RVC) in accordance with the invention and described in Example 2.

5

FIG. 3 shows a blank CV experiment without POM system at 60°C, 50 mV/S with the working electrode: 0.5 cm^2 RVC, CE: Platinum, RE: Ag/AgCl, described in Example 3.

10 FIG. 4 shows the Example 3 CV curves with different POM solution at 60°C with a scan rate of 50 mV/S with the working electrode: 0.5 cm^2 RVC, CE: Platinum, RE: Ag/AgCl.

Fig. 5 shows the effect of Nafion membranes on the performance of
15 POM/DMFC, 5 ml/min 1.0 M methanol, 180 ml/min 0.3M V3 POM, 500 ml in total MEA, RVC in the cathode, cell temperature: 77°C, referred to in Example 4

Fig.6 shows the effect of methanol concentration on the performance of
20 POM/DMFC, Nafion 117, E-Tek ½ MEA, RVC in the cathode, 2 ml/min methanol, 90 ml/min ~ 0.3 M V3 POM (total around 260 ml), cell temperature: 79-81°C, referred to in Example 5.

FIG. 7 shows a schematic diagram of a fuel cell constructed and arranged in accordance with the invention.

Referring to Fig. 7, there is shown the cathode side of fuel cell 1 in accordance with the invention comprising a polymer electrolyte membrane 2 separating an anode (not shown) from cathode 3. Cathode 3 comprises in this diagram reticulated carbon and is therefore porous. However other porous materials such as carbon felts and similar carbon fibre-based systems, as well as porous metal foams and grids and metal particles and metal oxide particles deposited on these porous materials. Polymer electrolyte membrane 2 comprises cation selective Nafion 115 membrane through which protons generated by the (optionally catalytic) oxidation of fuel (in this case methanol) in the anode chamber pass in operation of the cell, as schematically shown by the large arrows in FIG. 7. Electrons generated at the anode by the oxidation of fuel gas flow in an electrical circuit (not shown) and are returned to cathode 3. Fuel (in this case methanol) is supplied to the fuel passage of the anode chamber (not shown), while the oxidant (in this case air) is supplied to oxidant inlet 4 of cathode gas reaction chamber 5. Cathode gas reaction chamber 5 (the catalyst reoxidation zone) is provided with exhaust 6, through which the by-products of the fuel cell reaction (eg water and heat) can be discharged. The anode chamber is also provided with an exhaust for the carbon dioxide half reaction product in the anode region.

A catholyte solution comprising a catalyst and redox couple, in this case the oxidised form of the polyoxometallate provides both functions, is supplied in operation of the cell from catholyte reservoir 7 into the cathode inlet channel 8. The catholyte passes into reticulated carbon cathode 3,

5   which is situated adjacent membrane 2. As the catholyte passes through cathode 3, the polyoxometallate catalyst is reduced and is then returned to cathode gas reaction chamber 5 via cathode outlet channel 9.

Due to the advantageous composition of the catholyte of the present

10   invention, reoxidation of the catalyst occurs very rapidly, which allows the fuel cell to produce a higher sustainable current than with catholytes of the prior art.

Fuel, for example methanol, is passed against the first electrode (anode)

15   and, at the first electrode the following redox reaction occurs:

$$CH_3OH + H_2O \rightleftharpoons CO_2 + 6H^+ + 6e^-$$
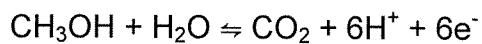
Electrons generated at the first electrode flow through the circuit, whilst

20   protons generated at the first electrode flow through the gas diffusion substrate and through the polymer electrolyte membrane towards the second electrode.

The fuel cell is provided with a reservoir 8 of a redox couple, which may be generally indicated as [R]. [R] may comprise for example a ferrous/ferric phenanthroline complex or a polyoxometallate complex has hereinbefore described, or may be any other suitable redox couple. In operation of the cell the oxidised redox material is passed against the second electrode and $[R]^{ox}$ ions are reduced to $[R]^{red}$ ions.

$$[R]^{ox} + ne^- \rightarrow [R]^{red}$$
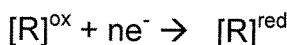
Water is also liberated in the gas reaction chamber in accordance with the following equation:

$$(4/n)[R]^{red} + O_2 + 4H^+ \rightarrow (4/n)[R]^{ox} + 2H_2O$$
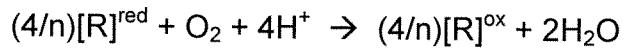
If peroxide is used as the oxidant instead of air or oxygen, then the reaction becomes:

$$(2/n)[R]^{red} + H_2O_2 + 2H^+ \rightarrow (2/n)[R]^{ox} + 2H_2O$$
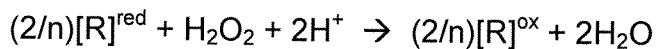
The reservoir is supplied in normal use of the cell with an oxidant material (for example air).

Preferably, the redox potential of the redox couple is less than about 0.6V, more preferably less than about 0.5V different from the potential of oxygen. For example the redox potential of the redox couple may be from

about 0.01V to about 0.6V, from about 0.01V to about 0.5V, or from about

0.01V to about 0.3V different from the potential of oxygen.

5   **Example 1**

A catholyte solution comprising $H_3Na_2PMo_9V_3O_{40}$ was prepared and

charged to the cathode chamber of a fuel cell generally in accordance with

that described with reference to FIG. 7.

10

The membrane electrode assembly (MEA) in this experiment comprised:

anode: JM PtRu black catalyst, 4.3 mg cm^{-2} and 10 % Nafion; cathode: 2.0

mm thick RVC + carbon veil. The anode gas diffusion layer was 10 %

teflonized carbon paper with 2 mg cm^{-2} XC-72 C and 10 % Nafion;

15 Membrane: Nafion 115; Area: 6.25 cm^2. Flow field: modified commercial

parallel anode and sink flow field in the cathode.

As shown in Fig. 1, the performance of a redox cathode in a DMFC using

a $H_3Na_3PMo_9V_3O_{40}$ POM system provides a maximum of power density at

20 80°C of about 40 mW cm^{-2}, which decreases with the temperature.

Example 2

The comparison, with reference to Figure 2, is shown of the redox cathode compared with a gas cathode. It can be seen that the redox cathode performs better, the performance of an air gas cathode at 60 °C is comparable to the redox cathode performance at 50 °C. The anode catalyst layer comprises 4 mg cm^{-2} PtRu black from JM and 10 wt % Nafion inside. The anode gas diffusion layer was 10 % teflonized carbon paper with 2 mg cm-2 XC-72 carbon and 10 % Nafion.

Example 3

Here, with reference to Figures 3 and 4, cyclic voltammetry is used to study the behaviour of methanol at the carbon electrode. A working electrode composed of 100 ppm RVC, used in the fuel cell studies was used. Current levels due to methanol were less than +/- 0.01 mA cm^{-2} in the range of potentials of operation of the fuel cell, which is a negligible current in comparison with the current densities of the fuel cell in operation. The CV of a low level of POM in the presence of methanol shows minimal impact in the range of operation of the fuel cell. Thus the impact of cross-over is limited at the electrode – no counter-current due to methanol oxidation occurs and there is little loss of the POM reduction.

Example 4

In this example similar cell, cathode and anode construction were used as for previous examples. Figure 5 shows a comparison in performance between nafion 117 at ~ 180 μ and nafion 115 at ~ 120 μ. It is clearly shown that the performance is better over nearly the whole current/voltage range, in contrast to the air cathode where nafion 117 is preferred due to the detrimental effects on performance of methanol crossover.

Example 5

In this example, with reference to Figure 6, was used a ½ MEA from Etek SERIES 12D-W MEA (5-layer) Half Membrane. Electrode Assembly for DMFC general purpose 5-layer, GDL base on woven web, in a similar cell and cathode to earlier examples using a modified commercial serpentine flow field for the anode. Other details are shown with the figure headings.

The benefit of using the fuel cell cathode of the invention is clear: there is no decrease in ocp with increasing methanol and little change in performance up to 8M MeOH, which contrasts strongly with air cathodes, where 1 M MeOH is preferred, and performance is weaker above 2 M methanol (Heinzel).

CLAIMS

1.   A fuel cell comprising an anode in an anode region of the cell and a cathode in a cathode region of the cell, the anode being separated from the cathode by an ion selective polymer electrolyte membrane, the anode region of the cell being supplied in use thereof with an alcoholic fuel, the cathode region of the cell being supplied in use thereof with an oxidant, the cell being provided with means for generating an electrical circuit between the anode and the cathode and with a non-volatile redox couple in solution in flowing fluid communication with the cathode in the cathode region of the cell, the redox couple being at least partially reduced at the cathode in operation of the cell, and at least partially re-generated by reaction with the oxidant after such reduction at the cathode, the redox couple and/or the concentration of the redox couple in the catholyte solution being selected so that the current density generated by the cell in operation is substantially unaffected by the oxidation of alcoholic fuel due to crossover of the alcoholic fuel from the anode region of the cell to the cathode region of the cell across the polymer electrolyte membrane.

2.   A fuel cell according to claim 1 wherein the alcoholic fuel comprises at least one low molecular weight alcohol.

3.   A fuel cell according to claim 2 wherein the alcoholic fuel is selected
        from methanol, ethanol, propanol, isopropanol and butanol,
        dipropylene glycol and ethylene glycol, and mixtures of two or more
        thereof.

4.   A fuel cell according to any one of claims 1 to 3 wherein the redox
        potential of the redox couple is from 0.01V to 0.3V different from the
        potential of oxygen.

5.   A fuel cell according to any one of claims 1 to 4 wherein the
        operating temperature of the fuel cell is below 100° C.

6.   A fuel cell according to any one of claims 1 to 5 wherein the redox
        couple comprises at least one transition metal complex.

7.   A fuel cell according to claim 6 wherein the redox couple comprises
        a polyoxometallate species.

8.   A fuel cell according to any one of claims 1 to 7 wherein the
        concentration of the redox couple in the catholyte solution is at least
        about 0.1M.

9.   A fuel cell according to any one of claims 1 to 8 wherein the cathode region of the cell is provided with a reservoir for storing the catholyte solution.

10.   A fuel cell according to any of claims 1 to 9 wherein the fuel cell is fitted with a switchable electronic valve to allow reverse flow of electrons along the connecting line when electromotive force is supplied to the fuel cell.

FIG. 1a
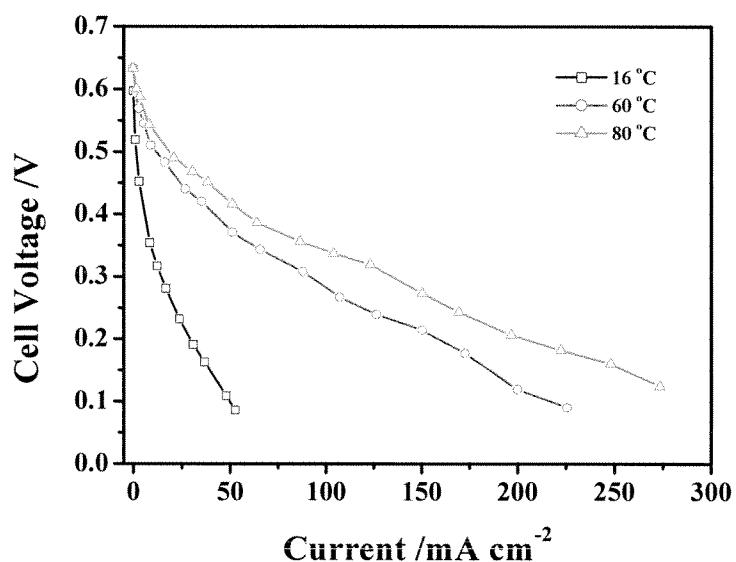
FIG. 1b
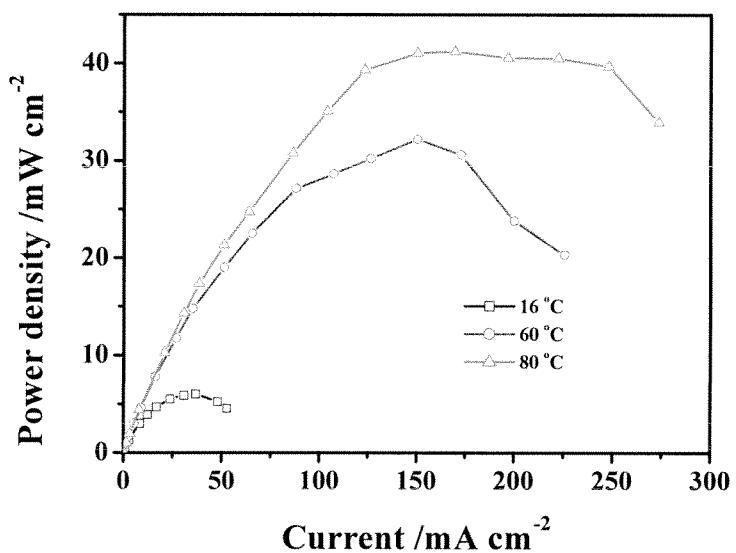
FIG. 2
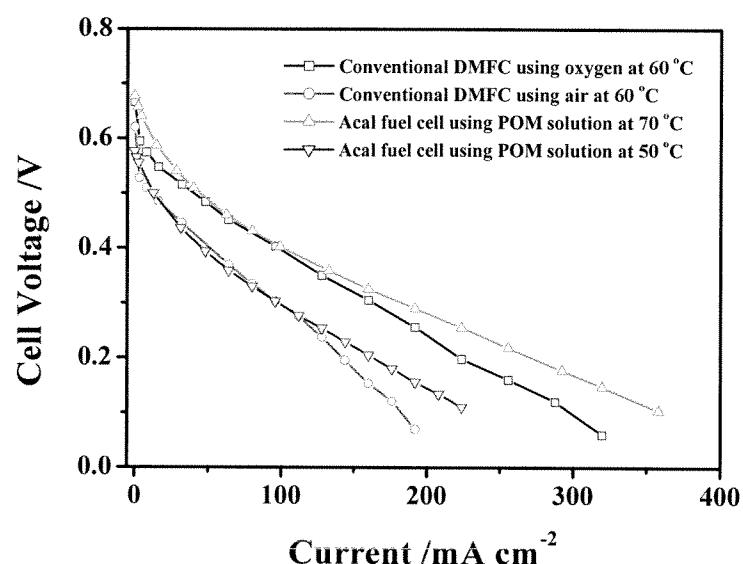
FIG. 3
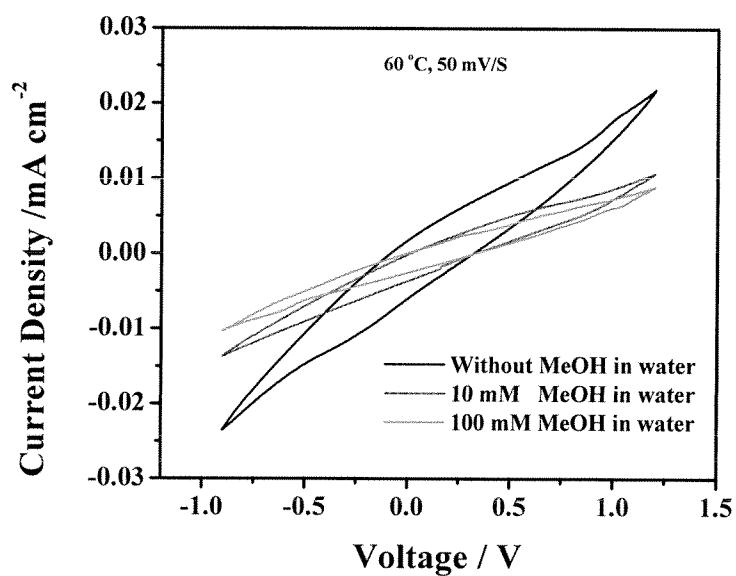
FIG. 4
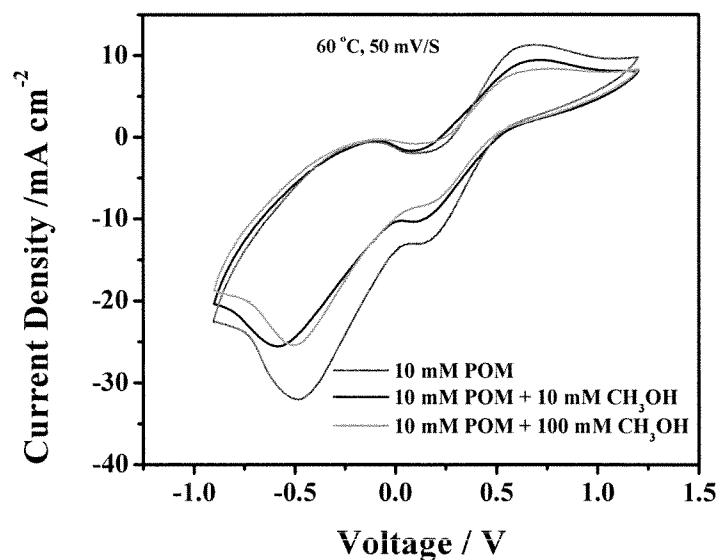
FIG.5
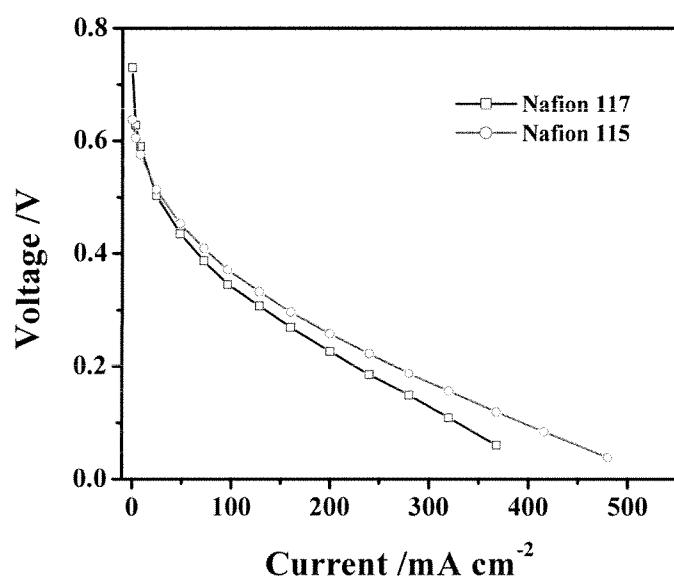
FIG. 6
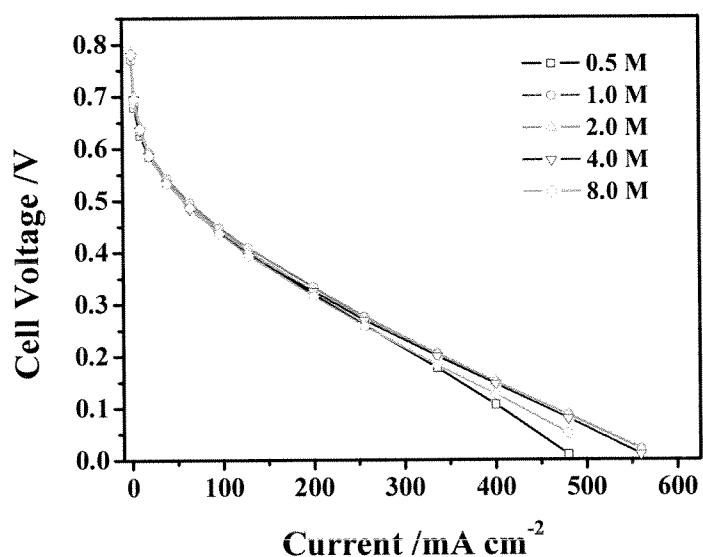
FIG. 7
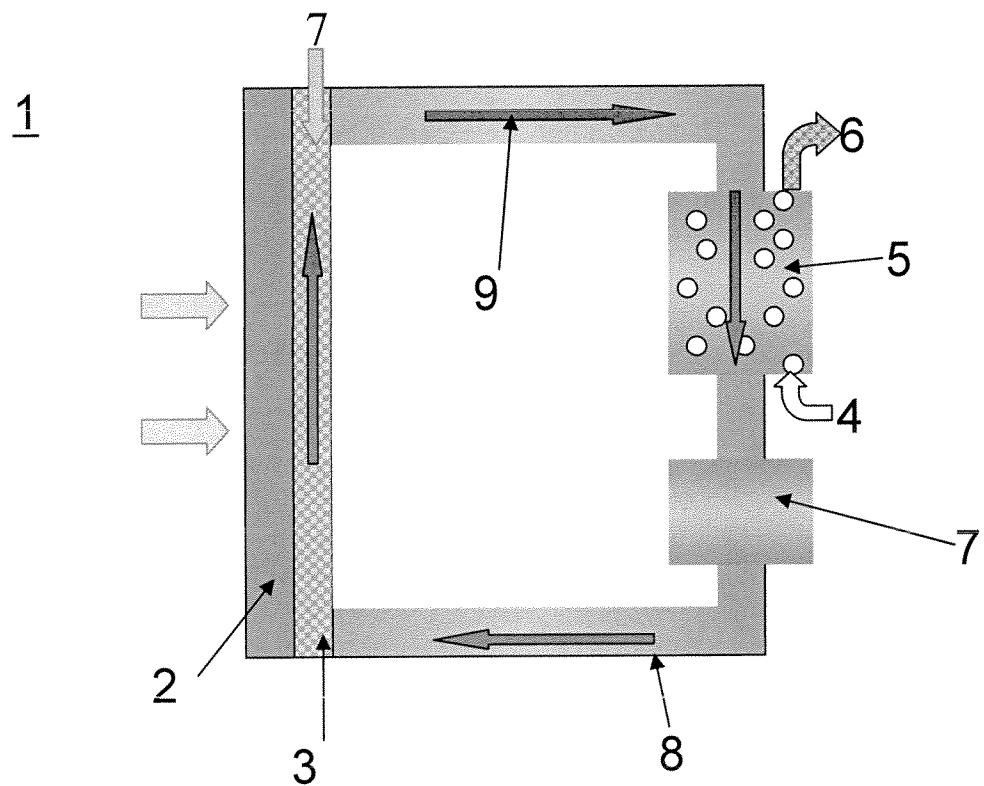
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M8/10   H01M8/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	GB 1 176 632 A (DU PONT [US]) 7 January 1970 (1970-01-07) page 1, line 50 - line 53 page 2, line 8 - line 13 page 2, line 62 - line 72 page 3, line 91 - line 111 page 4, line 4 - line 7 page 4, line 60 - line 62 -----	1-3,5,6, 8,10 4,7,10
Y	US 2005/112055 A1 (SHANNON CURTIS G [US] ET AL) 26 May 2005 (2005-05-26) paragraph [0006] paragraph [0009] paragraph [0052] ----- -/--	4,7,10

X	Further documents are listed in the continuation of Box C.		X	See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
4 July 2007	11/07/2007

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer MARTIN FERNANDEZ, A

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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P,X	WO 2006/097438 A (ACAL ENERGY LTD [GB]; CREETH ANDREW MARTIN [GB]) 21 September 2006 (2006-09-21) page 11, line 11 - line 12 page 4, line 7 - line 16 page 13, line 7 - line 8 page 23, line 9 - line 11	1-8
A	RU 2004 129396 A (GRINBERG VITALI A [RU] ET AL) 10 March 2006 (2006-03-10) & US 2007/078052 A1 (GRINBERG VITALI A [RU] ET AL) 5 April 2007 (2007-04-05)	1-10

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