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(54) Title: DIRECT FUEL REDOX FUEL CELLS

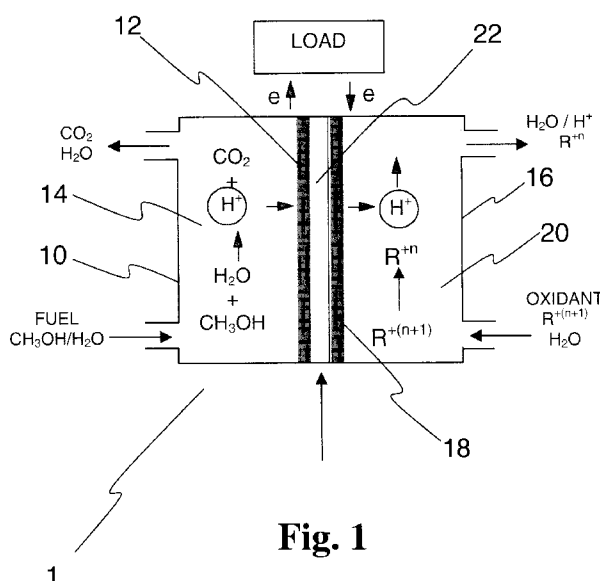


Fig. 1

(57) Abstract: The invention disclosed relates to direct fuel redox fuel cells employing high liquid fuel e.g. methanol, ethanol and formic acid, concentrations. A Direct Methanol Redox Fuel Cell (DMRFC) and a Direct Formic Acid Redox Fuel Cell (DFARFC) are disclosed. Polarization behaviour for these two systems is compared against a conventional Direct Methanol Fuel Cell (DMFC) and Formic Acid Fuel Cell (FAFC) under similar fuel concentrations. It was observed that conventional fuel cells with high liquid fuel concentrations suffer from fuel crossover and depolarization of the cathode, leading to a significant reduction in performance, whereas the redox based systems according to the invention, which contain no noble metal catalysts at the cathode, demonstrated an improvement in cell performance with higher fuel concentrations.



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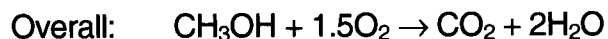
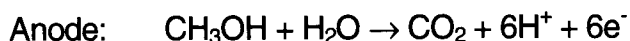
Direct Fuel Redox Fuel Cells

Field of the Invention

[001] This invention relates to direct-fuel fuel cells and in particular to direct fuel redox fuel cells, their use, and operation.

5 Background

[002] One type of fuel cell operating directly on liquid fuel ("direct-fuel fuel cell") is a direct methanol fuel cell (DMFC). There are many other known fuels that can also be used in a direct-fuel fuel cell, such as ethanol and formic acid. A DMFC is a type of proton exchange membrane fuel cell which
10 uses liquid methanol as a fuel and oxygen as an oxidant. The electrochemical reactions for this type of fuel cell are as follows:



15 [003] Direct-fuel fuel cells like the DMFC have some important advantages over conventional gaseous air / reformat proton exchange membrane (PEM) fuel cells. Such advantages include no separate humidification requirement, no separate cooling requirement, and no fuel processor which can potentially lead to significant simplification of the fuel cell and system.

20 However there are significant performance issues with the DMFC, which include methanol cross-over, water cross-over, and poor anode and cathode catalyst kinetics. Currently, platinum is typically used as a catalyst for both half reactions. This contributes to the loss of cell voltage potential, as any methanol that crosses over into the cathode chamber will oxidize and
25 deporalize the cathode. In one of the steps of the methanol oxidation reaction, a CO species is produced, which adsorbs strongly on the platinum catalyst, reducing the surface area for the catalyst reaction. Ruthenium is typically

added at the anode to counteract this problem, but ruthenium is expensive and adds to the cost of the fuel cell. Platinum is also very expensive and contributes to the high cost per kilowatt of the fuel cell.

[004] Present efforts to address the performance issues with the DMFC include attempts to reduce the methanol content of the fuel stream, to develop membranes that are more resistant to methanol cross-over, to develop more methanol-tolerant cathode catalysts, and to design the anode electrode structure to reduce methanol cross-over. To reduce the flooding effects of anode water cross-over, higher oxidant flow rates (stoichiometries) are generally used but with the penalty of higher system parasitic load. Also, all the standard approaches to mitigate cathode flooding are taken including flow field and electrode design. Much higher anode catalyst loadings are used for the DMFC anode (often > 10x) than for the standard hydrogen PEM fuel cell to improve reaction rates.

[005] Despite the benefits of liquid fed direct-fuel fuel cells, there is a need to reduce the cost and improve the performance of these systems. High Platinum Group Metal (PGM) catalyst loadings, used to compensate for poor reaction rate kinetics, are primarily responsible for high cost. Performance issues are related to poor reaction rate kinetics and more importantly fuel crossover from the anode to the cathode, which leads to both a fuel loss and depolarization of the cathode. Practically, this means that only lower concentrations of the fuel can be used (in order to reduce crossover) which reduces the reaction kinetics. Currently, low fuel concentrations or alternative membrane materials are used to help minimize fuel crossover.

[006] The issues with DMFC lead to cell performance about half of that for air / hydrogen or air / reformat PEM cells even at much larger precious metal catalyst loadings. At present the DMFC is targeted for micro fuel cell applications, which can support a much larger \$/kW cost. However, the lower performance and higher cost has prevented the DMFC from being widely adopted for larger scale applications. A breakthrough in DMFC performance and other direct-fuel fuel cells would have a significant impact on the fuel cell industry.

Summary of the Invention

[007] It is an object of this invention to provide a solution to at least some of the deficiencies in the prior art.

[008] According to one aspect of the invention, there is provided a method of operating a direct-fuel redox fuel cell comprising: supplying a catholyte to a platinum group metal (PGM)-free cathode of the fuel cell, wherein at least one of the catholyte and cathode includes a redox couple; and supplying an electroactive organic fuel to an anode of the fuel cell at a concentration between a concentration that does not result in fuel cross-over that has more than a 10% negative effect on voltage or a 24 mV voltage loss at any given current density, and a maximum stoichiometric concentration of the fuel.

[009] Alternatively, the fuel concentration can be in a range selected from the group consisting of: 2 M and a maximum stoichiometric concentration of the fuel; 4 M and a maximum stoichiometric concentration of the fuel; 6 M and a maximum stoichiometric concentration of the fuel; and 8 M and a maximum stoichiometric concentration of the fuel. The fuel can be selected from the group consisting of electroactive alcohols, electroactive organic acids, and electroactive ethers. In particular, the fuel can be one or combination of: propanol, methanol, formic acid, ethanol, dimethylether, dimethoxymethane, trimethoxy methane, and Trioxane. Specifically, the fuel can be an aqueous methanol solution in which case the maximum stoichiometric concentration is the equimolar methanol / water stoichiometric amount of 16.7 M. Alternatively, the fuel can be an aqueous formic acid solution in which case the maximum stoichiometric concentration is the equimolar formic acid / water stoichiometric amount of 18 M. Or, the fuel can be pure formic acid in which case the maximum stoichiometric concentration is 26.5 M.

[0010] The redox couple can be selected from the group consisting of: metal ions, organic redox couples, and complexed metal ions. In particular, the redox couple can be selected from the group consisting of: ferrous / ferric

ions ($\text{Fe}^{+2} / \text{Fe}^{+3}$); $\text{Fe}(\text{phenanthroline})_3^{3+} / \text{Fe}(\text{phenanthroline})_3^{2+}$; $\text{VO}_2^+ / \text{VO}^{2+}$; and o-Toluidine ($\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$) / (o-Toluidine) $^-$, and $\text{Ce}^{4+} / \text{Ce}^{3+}$.

[0011] The method can further comprise the step of regenerating a reduced redox couple using a regenerator selected from the group consisting of: a chemical regenerator, electrochemical regenerator, a photochemical regenerator and combinations thereof. In particular, the regenerator can be a chemical regenerator comprising active carbon catalyst.

[0012] Instead of a regenerator, the fuel cell can be operated such that the catholyte is discharged from the cathode without regeneration of the redox couple. Such application can be found, for example, in single use or "disposable" applications.

[0013] The catholyte can comprise an aqueous redox couple catholyte solution. Alternatively or additionally, at least some of the redox couple can be attached to the cathode surface.

[0014] Another aspect of the invention relates to the use of a direct fuel redox fuel cell at a fuel concentration between a concentration that does not result in a fuel cross-over that has more than a 10% negative effect on overall voltage performance at a given current density, and a maximum stoichiometric concentration of the fuel, wherein the fuel cell comprises a platinum group metal (PGM)-free cathode assembly. In such use, the fuel can be selected from the group consisting of methanol, formic acid, ethanol, dimethylether, dimethoxymethane, trimethoxy methane, and Trioxane.

Brief Description of the Drawings

[0015] **Figure 1** is a schematic of a liquid fuel fed direct methanol redox fuel cell (DMRFC) according to an embodiment of the invention.

[0016] **Figures 2 and 3** respectively illustrate the components of a prior art DMFC and the DMRFC of Figure 1 using methanol as the liquid fuel.

[0017] **Figures 4 and 5** respectively illustrate the components of a prior art formic acid fuel cell (FAFC) and a formic acid redox fuel cell (FARFC) using formic acid as the liquid fuel.

5 [0018] **Figure 6** is a graph illustrating the effect of fuel concentration on DMFC and DMRFC fuel cell performance.

[0019] **Figure 7** is a graph illustrating the effect of fuel concentration on FAFC and FARFC fuel cell performance.

[0020] **Figure 8** is a schematic of a column reactor for chemically regenerating oxidized redox oxidant.

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Detailed Description of Embodiments of the Invention

[0021] The embodiments of the invention described herein relate to direct fuel redox fuel cells (DFRFC) which uses a redox couple as a catholyte at the cathode of the fuel cell, and methods of operating same.

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[0022] The DFRFC is designed to use high concentrations of liquid electroactive organic fuel (e.g. methanol, ethanol, formic acid) without leading to a decrease in performance. In particular, the DFRFC does not use platinum group metal (PGM) catalyst since redox couples do not require a PGM catalyst at the cathode for acceptable reaction rate kinetics; further, catalytic materials for the redox couple such as carbon are selective to the redox couple only. The absence of PGMs at the cathode precludes depolarization of the cathode by fuel crossover and combustion since methanol can only be oxidized over PGMs. Furthermore, the DFRFC is embodied in either a single pass type fuel cell wherein the redox couple is passed through the fuel cell once and is not regenerated (e.g. for disposable cartridge applications), or the redox couple is regenerated using regenerators which are tolerant to the high fuel concentrations, such as chemical, photochemical and electrochemical regenerators.

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[0023] Therefore, the DFRFC can operate using a range of fuel concentrations that would otherwise tend to cause significant cross-over of fuel which would cause a cathode to depolarize in a conventional (non-redox) direct-fuel fuel cell, and to harm micro-organisms in known microbial redox couple regenerators. In the embodiments of the present invention, such higher fuel concentrations can be introduced to improve mass transfer and reaction rate kinetics at the anode without introducing additional complications.

[0024] Referring to Figures 1 and 3 and according to a first embodiment of the invention, the DFRFC 1 can be a direct methanol redox fuel cell (DMRFC) which uses a redox couple for the catholyte in combination with a liquid methanol fuel anolyte. The DMRFC 1 includes an anode assembly 10 containing an anode 12 and an anolyte flow field 14 for flowing an anolyte solution (fuel) to the anode 12; a cathode assembly 16 containing a cathode 18 and a catholyte flow field 20 for flowing a catholyte solution to the cathode 18, and a PEM 22 sandwiched between the anode 12 and cathode 18. It is noted that although a PEM is used in this embodiment, other types of ionically conductive electrolyte separators can be used, depending on the fuel and as known to one skilled in the art.

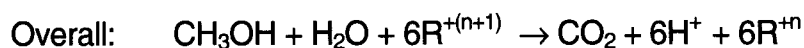
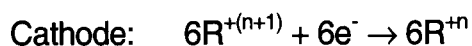
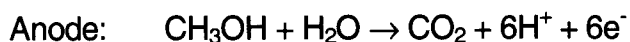
[0025] The anode flow field 14 is a separator plate with a flow channel extending across the face of the separator plate 14 facing the anode 12; the flow channel can have a serpentine configuration as shown in Figure 3, or have another configuration as is known in the art for DMFC anodes. The anode 12 comprises Pt / Ru anode catalyst on porous carbon fiber paper. The PEM 22 can be any suitable membrane known for use with direct fuel cells, and for example, can be a Nafion 117 membrane.

[0026] The cathode flow field 20 is a separator plate having a recessed pocket in the face of the separator plate facing the cathode 18. The cathode 18 is a sheet of porous carbon fiber paper. Preferably, the cathode for the redox couple is a non-noble metal material such as carbon, which will not catalyze oxidation of methanol, i.e., it is selective to the redox couple only.

Alternatively, the cathode can be made from any suitable chemically inert electrically conducting material as known in the art, such as nickel and stainless steel. To avoid catalytic depolarization, platinum group metals are excluded from the cathode assembly.

5 [0027] The anode assembly 10 is provided with a fuel supply manifold (not shown) having an inlet, which supplies aqueous methanol fuel to the flow channels of the anode separator plate 14 and an outlet which removes spent fuel from the anode assembly 10. The cathode assembly 16 is provided with a redox
10 oxidant manifold (not shown) having an inlet which supplies an aqueous redox oxidant to the pocket of the cathode separator plate 20, and an outlet which removes spent redox oxidant from the cathode assembly 16. Examples of suitable redox oxidants include metal ions, e.g., Fe^{+3} , which can be provided as an electrolyte soluble salt, e.g. $\text{FeNH}_4(\text{SO}_4)_2$. Examples of other suitable redox couples are provided later in this description.

15 [0028] The chemical reactions for the DMRFC 1 can be summarized as follows:



20 [0029] Regeneration of oxidant: $6\text{R}^{+n} + 6\text{H}^+ + 1.5\text{O}_2 = 6\text{R}^{+(n+1)} + 3\text{H}_2\text{O}$

[0030] As seen in the reaction equations above, spent redox oxidant includes reduced oxidant that must be regenerated (oxidized) before being used again in catholyte. The regeneration function could be integrated into the cathode assembly. (to increase gravimetric and volumetric power density) or could be a
25 separate system reactor that is in the recirculation loop of the catholyte for the fuel cell.

[0031] In this embodiment, and referring to Figure 8, a chemical regenerator 22 is fluidly coupled to the inlet and outlet of the cathode oxidant manifold and is

used to oxidize the redox oxidant that was reduced in the cathode. A suitable chemical regenerator is a column reactor with static packing elements containing catalyst particles, such as Katapak S reactor elements where wire gauze is used to hold small catalyst particles. When an aqueous ferrous / ferric ion ($\text{Fe}^{+2} / \text{Fe}^{+3}$) redox couple catholyte solution is used as the redox oxidant in the DMRFC, a suitable catalyst is active carbon that is packed in Katapak S reactor elements. Such a chemical regenerator is operated at an elevated oxygen pressure of 4.7 Bar and temperature of 120 °C, with a catalyst packing density of 7.1 – 142 Kg catalyst / m³.

[0032] Alternatively, the chemical regenerator 22 can be a batch, continuous slurry and packed bed type reactor.

[0033] Instead of a chemical regenerator, other types of regenerators or combinations thereof can be used as is known in the art, such as electrochemical regenerators and photochemical regenerators.

[0034] When oxygen oxidant in a DMFC is replaced by a redox oxidant (R) as in a DMRFC 1, the rate of the cathode reaction and the rate of mass transfer of the oxidant to the electrode surface is increased by several orders of magnitude compared to oxygen. Better mass transport is due to the much higher aqueous solubility of the oxidant in redox fuel cells compared to oxygen.

[0035] While methanol cross-over is undesirable from a fuel efficiency point of view it will not depolarize the cathode in a DMRFC. In general, one would like to achieve the maximum possible concentration of liquid fuel, without introducing other issues, such as corrosion. Accordingly, concentrations of liquid fuels beginning at the upper limit of the conventionally accepted range fuel concentration for direct-fuel fuel cells, up to the maximum stoichiometric concentration of the fuel could be used in the DMRFC 1 according to this embodiment, which would improve performance and system requirements, and improve fuel storage capability. The conventionally accepted upper limit of fuel concentration for direct-fuel fuel cells is a concentration that does not result in fuel cross-over that has more than a 10% negative effect on voltage or a 24 mV voltage loss at any given current density. As cross-over does not present

problems to the cathode or an optional regenerator in the DMRFC 1, operating at fuel concentrations at or above this limit does not pose a problem to the DMRFC 1.

[0036] For conventional direct methanol fuel cells, the industry-accepted upper limit of fuel concentration is about 1 to 2 M methanol in aqueous solution; any higher concentration will result in a rate of methanol cross-over that would depolarize conventional DMFC catalyst and harm micro-organisms in known microbial redox couple regenerators to an extent that makes practical application of DMFC unfeasible. For a Nafion 117 PEM, the maximum methanol concentration in a conventional DMFC should be less than 1 M (corresponds to 3 % by weight) to minimize the effect of methanol cross-over; even at this concentration methanol crossover is appreciable, about 20%.

[0037] For methanol, stoichiometry indicates that the maximum concentration is 16.7 M, which represents an equimolar solution of water and methanol. The water cross-over and associated flooding issues in air electrodes would not be an issue with the liquid redox catholyte electrode, i.e., it is a flooded electrode. However, water cross-over could result in some dilution of the redox electrolyte.

[0038] Therefore, and as supported in the experimental results described below, the fuel concentration range for the DMRFC 1 of the present embodiment can be between 2 M and 16.7 M. According to an alternative embodiment of the invention, the methanol concentration range for the DMRFC 1 can be one of 4 M to 16.7 M; 6 M to 16.7 M; and 8 M to 16.7 M.

[0039] According to a second embodiment of the invention and referring to Figure 5, the DFRFC 1 can be a direct formic acid redox fuel cell (DFARFC) which uses a redox couple for the catholyte in combination with a liquid formic acid fuel anolyte. Like the DMRFC 1, the DFARFC 1 includes an anode assembly 10 containing an anode 12 and an anolyte flow field 14 for flowing an anolyte solution to anode; a cathode assembly 16 containing a cathode 18 and a catholyte flow field 20 for flowing a catholyte solution to the cathode, and a PEM 22 [sandwiched between the anode 12 and cathode 18. Like the

first embodiment, another type of ionically conductive electrolyte separator could be used for different fuels as is known to one skilled in the art.

[0040] Also like the DMRFC 1 of the first embodiment, the DFARFC cathode flow field 20 is a separator plate having a recessed pocket in the face of the separator plate facing the cathode 18. However, the cathode 18 comprises a multi-layer porous carbon fiber paper.

[0041] Like the DMRFC 1, concentrations of liquid fuel up to the stoichiometric amount required for the reaction could be used which would improve performance and the system water requirements. Where formic acid is used as the liquid fuel, stoichiometry permits the use of pure formic acid, and thus the fuel concentration could be as high as 26.5M.

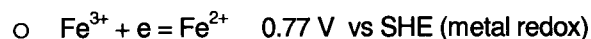
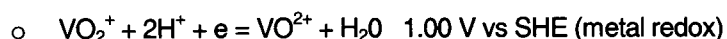
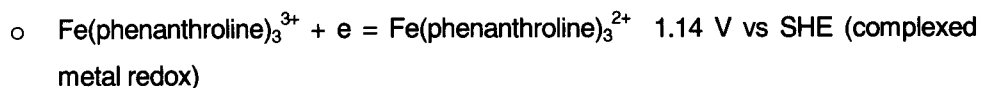
[0042] According to another embodiment of the invention, there is provided a direct fuel redox fuel cell which comprises a single pass catholyte flow field. That is, the redox couple fed into the cathode assembly and reacted at the cathode is not regenerated; the reduced redox oxidant is discharged from the fuel cell. Otherwise, the fuel cell is identical to the embodiments previously described. When employing methanol as the fuel, the fuel cell resembles that shown in Figure 1 and 3, and when employing formic acid as the fuel, the fuel cell resembles that shown in Figure 5. Such a fuel cell is expected to be employed in disposable applications, and can be packaged for example as a single use cartridge that will be discarded once the fuel and oxidant are exhausted. Because there are no biological material nor PGM catalysts in the cathode assembly, the direct methanol redox fuel cell can be operated at methanol concentrations between 2 M up to the maximum stoichiometric concentration for methanol, or alternatively between one of 2M and 16.7 M, 4M and 16.7M, 6M and 16.7 M, and 8 M and 16.7 M methanol. Alternatively, the direct redox fuel cell can be operated with any concentration of formic acid up to the up to 26.5 M with the balance being water or other solvents.

[0043] The DMRFC and DFARFC embodiments as described above are only a few ways to design a direct fuel redox fuel cell. Many possible design variations are possible which would not be possible in conventional fuel cell

technology, e.g., the Direct Methanol Fuel Cell, etc. Some possible design variations are as follows:

- Although this application discusses direct liquid methanol and formic acid fuels, other electro-organic fuels are possible and may have some advantages over methanol such as reduced cross-over due to steric hindrance effects or catalyst selectivity, etc. For example, other direct fuels could include ethanol, dimethylether (DME), dimethoxymethane (DMM), trimethoxy methane (TMM), Trioxane, etc (J.T. Muller, P.M. Urban, W.F. Holderich, K. Colbow and D.P. Wilkinson, J. of the Electrochemical Society, 147 (11), 4058 (2000)), the disclosure of which is incorporated herein by reference.

- Although metal ions have mainly been targeted here for the redox system in the DMRFC 1 it is possible to use organic redox couples or complexed metal ions (e.g., metallocenes) which may provide a better selection of voltage potentials, and may prevent or significantly reduce redox cross-over to the anode due to steric hindrance effects, etc. One would expect complexation to have some impact on the kinetics of the electron transfer reaction. Some types of redox couples include ferrous / ferric ions ($\text{Fe}^{+2} / \text{Fe}^{+3}$); $\text{Fe}(\text{phenanthroline})_3^{3+} / \text{Fe}(\text{phenanthroline})_3^{2+}$; $\text{VO}_2^+ / \text{VO}^{2+}$; and o-Toluidine ($\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$) / (o-Toluidine) $^-$, and $\text{Ce}^{4+} / \text{Ce}^{3+}$. Exemplary reactions are shown as follows:



- For chemical regeneration by oxygen, the redox couple should have adequate solubility in the electrolyte, and the reduction potential should be as high as possible but below the oxidant (for regeneration) reduction potential (e.g., for $\text{O}_2 < 1.23$ V vs SHE). Also, some of the redox couple

types could be attached (fixed) to the electrode surface, e.g., the modified electrode approach.

- Depending on the choice of redox system it may be possible to use a non-aqueous solvent system for the catholyte that is immiscible with the electro-organic fuel and hence prevents the issue with fuel cross over and loss of fuel efficiency.
- Membrane development and membrane surface functionality could be specific to the DMRFC 1 to prevent fuel and redox species cross-over.
- As a result of the elimination of the need for a 3 phase zone at the cathode (compared to O_2 reduction) or a complicated flow field this can lead to simplification of the overall design. For example, the cathode does not need to be in contact with the membrane.

Example

(a) Experiment

[0044] Both methanol (CH_3OH) and formic acid ($HCOOH$) liquid fuels were studied and compared in a 4 cm^2 PEM fuel cell using a conventional air cathode as shown in Figure 2 to form a conventional DMFC, using a redox couple cathode to form a DMRFC according to the embodiment described above and as shown in Figures 1 and 3, using a conventional air cathode as shown in Figure 4 to form a conventional $HCOOH$ fuel cell (DFAFC), and using a redox couple cathode to form a $HCOOH$ redox fuel cell (DFARFC) according to the embodiment described above and as shown in Figure 5.

[0045] Both conventional direct methanol and formic acid fuel cells and direct methanol and formic acid redox fuel cells used an anode separator plate having a serpentine flow channel for flow of an anolyte solution therethrough, an anode having Pt / Ru anode catalyst on carbon fiber paper, and a Nafion 117 PEM. The use and construction of such fuel cell components are well known in the art and not described in detail here.

[0046] Both conventional direct methanol and formic acid fuel cells used a conventional cathode separator plate having a serpentine flow field and a cathode having Pt cathode catalyst on carbon fiber paper. In contrast, both the direct methanol and direct formic acid redox fuel cells used a cathode separator plate having a square recess with a depth of 1 mm, and a Pt-free carbon fiber paper cathode placed in the square recess; the DMRFC used a single layer of such carbon fiber paper, whereas the DFARFC used a six layer carbon fiber paper cathode.

[0047] Aqueous methanol fuel solution was supplied to the serpentine flow channel in the anode separator plate for both the conventional DMFC and the DMRFC according to the present embodiment. Air was supplied to the flow channel in the cathode separator plate for the DMFC and an aqueous ferrous / ferric ion ($\text{Fe}^{+2} / \text{Fe}^{+3}$) redox couple catholyte solution was supplied to the recess of the cathode separator plate in the DMRFC.

[0048] Similarly, aqueous formic acid fuel solution was supplied to the serpentine flow channel in the anode separator plate for both the conventional DFAFC and the DFARFC. Air was supplied to the flow channel in the cathode separator plate for the DFAFC and an aqueous ferrous / ferric ion ($\text{Fe}^{+2} / \text{Fe}^{+3}$) redox couple catholyte solution was supplied to the pocket of the cathode separator plate in the DFARFC.

[0049] Each fuel cell was tested at a conventional "low" fuel concentration (2 M) and a novel "high" fuel concentration corresponding to equimolar fuel and water (16.7M methanol, 18 M formic acid). An even higher concentration of formic acid (26.5 M) is possible because fuel oxidation does not require water. Thus four systems can be identified: the DMFC, DMRFC, DFAFC and DFARFC. The redox couple was kept at a constant concentration of 0.9 M total Fe. Slightly higher concentrations (1M) are possible, but precipitation of the electroactive species may be an issue above 0.9M. In general, the concentration range should be less than the limit for saturation and therefore, precipitation. The electrochemical reactions of each system are outlined in

Figures 2-5. Half cell reaction potentials are given relative to the Standard Hydrogen Electrode (SHE).

(b) Results and Discussion

[0050] Polarization curves (Potential vs. Current Density) were generated for each system and fuel concentration.

[0051] The results for systems employing methanol and formic acid are presented in Figures 6 and 7, respectively. More specifically, figure 6 illustrates effect of fuel concentration on DMFC and DMRFC fuel cell performance, the reactants and components are included in Tables 1 and 2.

Table 1**Direct Methanol Fuel Cell (DMFC)**

cell temperature= 70°C

cell area= 4 cm²

membrane= Nafion 117

Anode

reactant stoich= 4

anolyte= (2 M or 16.7 M CH₃OH), 0.5 M H₂SO₄

electrode= non-wetproof carbon fiber paper

catalyst= 2 mg/cm² 40% Pt/Ru supported on carbon**Cathode**

reactant stoich= 4

catholyte= air at 100 kPa

electrode= non-wet proof carbon fiber paper

catalyst= 1 mg/cm² 40% Pt on carbon**Table 2****Direct Methanol Redox Fuel Cell (DMRFC)**

cell temperature= 70°C

cell area= 4 cm²

membrane= Nafion 117

Anode

reactant stoich= 4

anolyte= (2 M or 16.7 M CH₃OH), 0.5 M H₂SO₄

electrode= non-wetproof carbon fiber paper

catalyst= 2 mg/cm² 40% Pt/Ru supported on carbon**Cathode**

reactant stoich= 4

catholyte= 0.81 M FeNH₃(SO₄)₂, 0.09 M FeSO₄,
0.405 M H₂SO₄

electrode= non-wet proof carbon fiber paper

catalyst= none

[0052] Figure 7 illustrates Effect of fuel concentration on DFAFC and DFARFC fuel cell performance, the reactions and cell components are included in Tables 3 and 4.

Table 3**Formic Acid Fuel Cell (FAFC)**

cell temperature= 70°C

cell area= 4 cm²

membrane= Nafion 117

Anode

reactant stoich= 4

anolyte= (2 M or 18 M HCOOH), 0.5 M H₂SO₄

electrode= non-wetproof carbon fiber paper

catalyst= 2 mg/cm² 40% Pt/Ru supported on carbon**Cathode**

reactant stoich= 4

catholyte= air at 100 kPa

electrode= non-wet proof carbon fiber paper

catalyst= 1 mg/cm² 40% Pt on carbon**Table 4****Formic Acid Redox Fuel Cell (FARFC)**

cell temperature= 70°C

cell area= 4 cm²

membrane= Nafion 117

Anode

reactant stoich= 4

anolyte= (2 M or 18 M HCOOH), 0.5 M H₂SO₄

electrode= non-wetproof carbon fiber paper

catalyst= 2 mg/cm² 40% Pt/Ru supported on carbon**Cathode**

reactant stoich= 4

catholyte= 0.81 M FeNH₃(SO₄)₂, 0.09 M FeSO₄,
0.405 M H₂SO₄

electrode= non-wet proof carbon fiber paper

catalyst= none

[0053] Although the above experiments were all effected at 70°C, the system was tested between room temperature and 70°C. In general for

aqueous systems, the operating temperature would depend upon the redox couple being used, and would generally lie between room temperature and 90°C, noting that hydrolysis would occur at higher temperatures.

[0054] Similar trends were observed for both the methanol and formic acid based systems. Firstly, conventional configurations incorporating a low fuel concentration and an air cathode containing PGM catalyst exhibited the best overall performance. However, the performance of these conventional systems dropped by more than 50% when fed with a high concentration fuel. The Open Circuit Voltage (OCV), taken at zero current, can provide some insight to the severity of cathode depolarization due to fuel crossover. Since no current is being drawn at this point, the only significant factor that can reduce the cell potential is direct combustion of the fuel and oxidant at the cathode due to fuel crossover. It can be seen in Figures 6 and 7 that the OCV of conventional systems fed with high concentration fuel is approximately half of its normal value, indicating that fuel crossover and combustion has caused the cathode to depolarize.

[0055] On the other hand, the OCV of redox based systems is not negatively affected by high fuel concentrations. Instead, the advantages of using a high fuel concentration are observed through enhanced cell performance, likely as a result of improved reaction kinetics and improved mass transport at the anode. In particular, it is expected that other high fuel concentrations such as: greater than 2 M, 4 M, 6 M, 8 M, 10 M, 12 M, and 14 M will enjoy the performance advantages as found for the 16.7 M CH₃OH and 18 M HCOOH experiments. This is a trend that appears to have not been disclosed before for fuel cells operating on liquid fuels directly; consequently, the DMRFC and DFARFC represent a new type of fuel cell that is not limited in fuel concentration nor plagued by fuel crossover performance issues but has the advantage of using non-PGM material on the cathode with good performance. Many variations involving different liquid fuels or redox couples could be conceived to achieve an analogous system possessing the aforementioned advantages.

[0056] Conventional fuel cells operating on liquid fuels suffer from cathode depolarization by methanol crossover and combustion. The fuel concentration is typically kept below 1-2 M to minimize crossover; however, this has secondary negative effects on the cell's performance. The redox based systems reported here are not susceptible to cathode depolarization and can accommodate high fuel concentrations. It has been shown that although conventional systems exhibit a decrease in overall cell performance with increasing fuel concentration, the redox based systems demonstrate improved cell performance at high fuel concentrations. Such systems represent a new type of fuel cell and can employ a wide variety of liquid fuels or redox couples.

[0057] One or more currently preferred embodiments have been described by way of example. It will be apparent to persons skilled in the art that a number of variations and modifications can be made without departing from the scope of the invention as defined in the claims.

What is claimed is:

1. A method of operating a direct-fuel redox fuel cell comprising:

supplying a catholyte to a platinum group metal (PGM)-free cathode of the fuel cell, wherein at least one of the catholyte and cathode includes a redox couple; and

supplying an electroactive organic fuel to an anode of the fuel cell at a concentration between a concentration that does not result in fuel cross-over that has more than a 10% negative effect on voltage or a 24 mV voltage loss at any given current density, and a maximum stoichiometric concentration of the fuel.

2. A method as claimed in claim 1 further comprising supplying the fuel to the anode at a concentration range selected from the group consisting of: 2 M and a maximum stoichiometric concentration of the fuel; 4 M and a maximum stoichiometric concentration of the fuel; 6 M and a maximum stoichiometric concentration of the fuel; and 8 M and a maximum stoichiometric concentration of the fuel.

3. A method as claimed in claim 2, wherein the fuel is selected from the group consisting electroactive alcohols, electroactive organic acids, and electroactive ethers.

4. A method as claimed in claim 3 wherein the fuel is selected from the group consisting of propanol, methanol, formic acid, ethanol, dimethylether, dimethoxymethane, trimethoxy methane, and Trioxane.

5. A method as claimed in claim 4 wherein the fuel is aqueous methanol solution and the maximum stoichiometric concentration is the equimolar methanol / water stoichiometric amount of 16.7 M.

6. A method as claimed in claim 4 wherein the fuel is aqueous formic acid solution and the maximum stoichiometric concentration is the equimolar formic acid / water stoichiometric amount of 18 M.

7. A method as claimed in claim 4 wherein the fuel is pure formic acid and the maximum stoichiometric concentration is 26.5 M.

8. A method as claimed in claim 1 wherein the redox couple is selected from the group consisting of: metal ions, organic redox couples, and complexed metal ions.

9. A method as claimed in claim 8 wherein the redox couple is selected from the group consisting of: ferrous / ferric ions (Fe^{+2} / Fe^{+3}); $\text{Fe}(\text{phenanthroline})_3^{3+}$ / $\text{Fe}(\text{phenanthroline})_3^{2+}$; VO_2^+ / VO^{2+} ; and o-Toluidine ($\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$) / (o-Toluidine) $^-$, and Ce^{4+} / Ce^{3+} .

10. A method as claimed in claim 9 further comprising regenerating a reduced redox couple using a regenerator selected from the group consisting of one or a combination of: a chemical regenerator, electrochemical regenerator, and a photochemical regenerator.

11. A method as claimed in claim 10 wherein the regenerator is a chemical regenerator comprising active carbon catalyst.

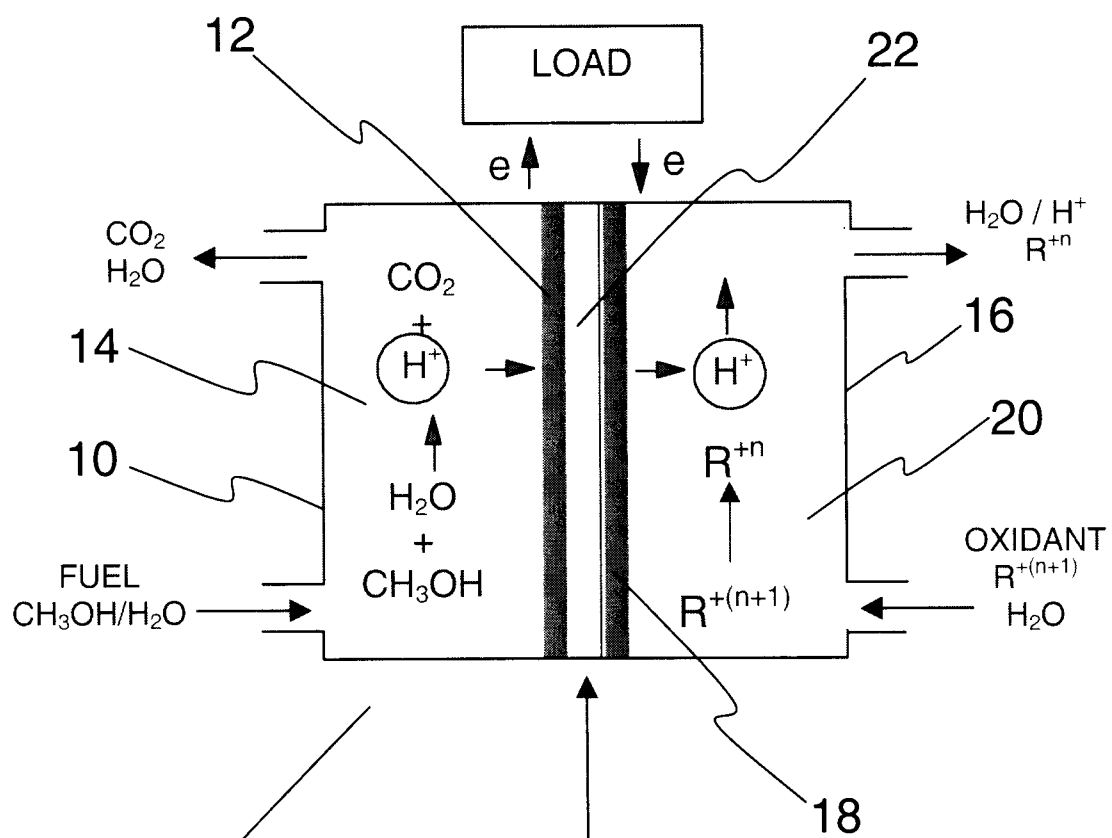
12. A method as claimed in claim 1 wherein the catholyte is discharged from the cathode without regeneration of the redox couple.

13. A method as claimed in claim 1 wherein the catholyte comprises an aqueous redox couple catholyte solution.

14. A method as claimed in claim 1 wherein at least some of the redox couple are attached to the cathode surface.

15. Use of a direct fuel redox fuel cell at a fuel concentration between a concentration that does not result in fuel cross-over that has more than a 10% negative effect on voltage or a 24 mV voltage loss at any given current density, and a maximum stoichiometric concentration of the fuel, wherein the fuel cell comprises a platinum group metal (PGM)-free cathode assembly.

16. Use of a direct fuel redox fuel cell as claimed in claim 15 wherein the fuel is selected from the group consisting of methanol, formic acid, ethanol, dimethylether, dimethoxymethane, trimethoxy methane, and Trioxane.

**Fig. 1**

1

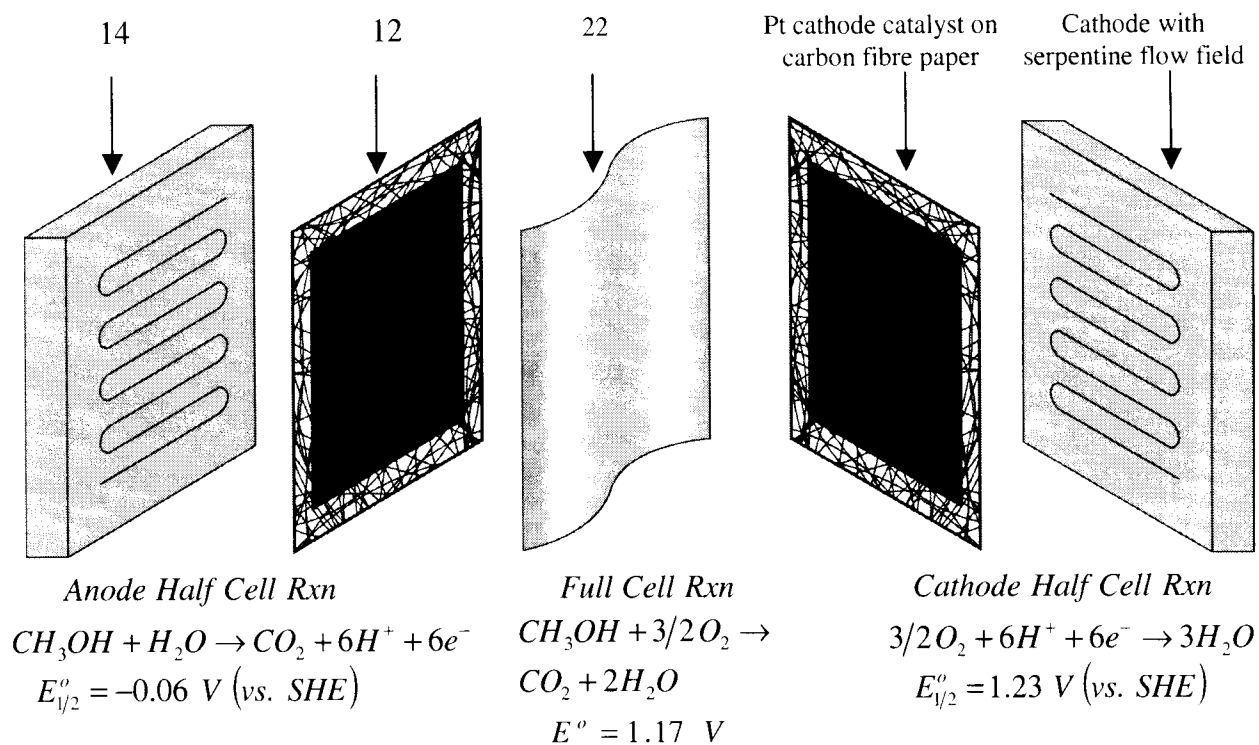


Fig. 2(Prior Art)

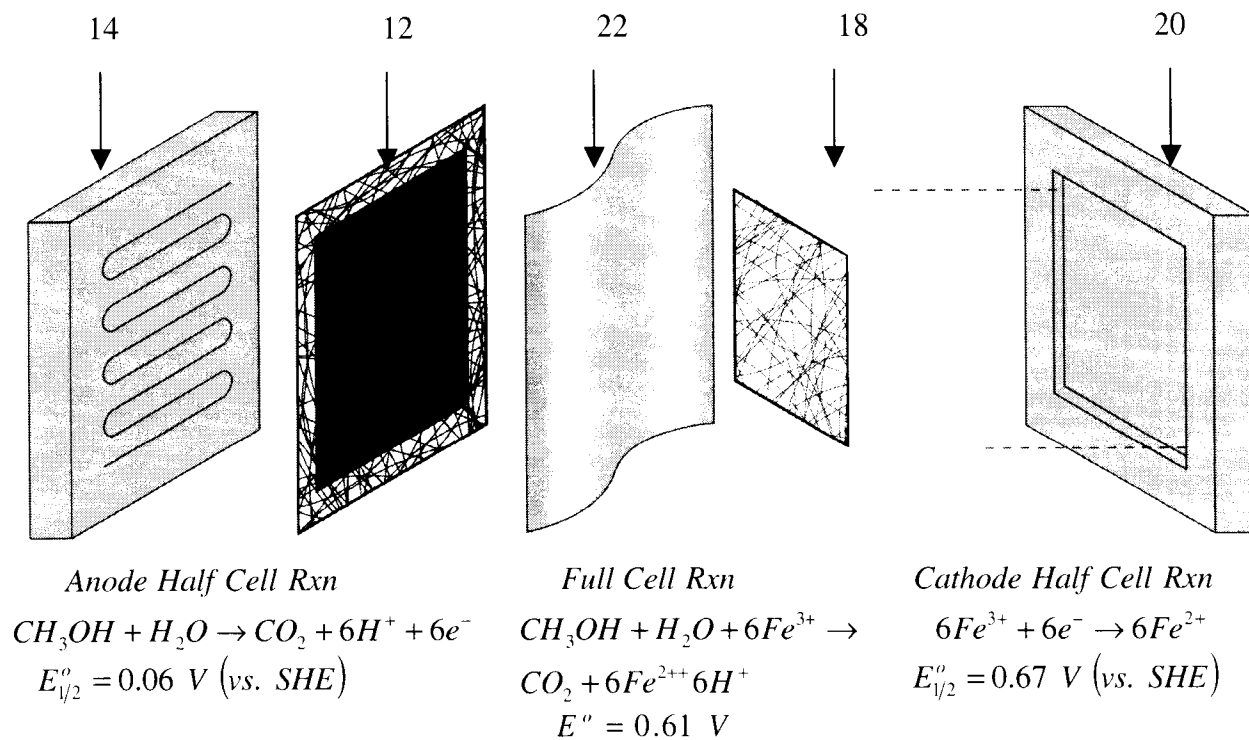


Fig. 3

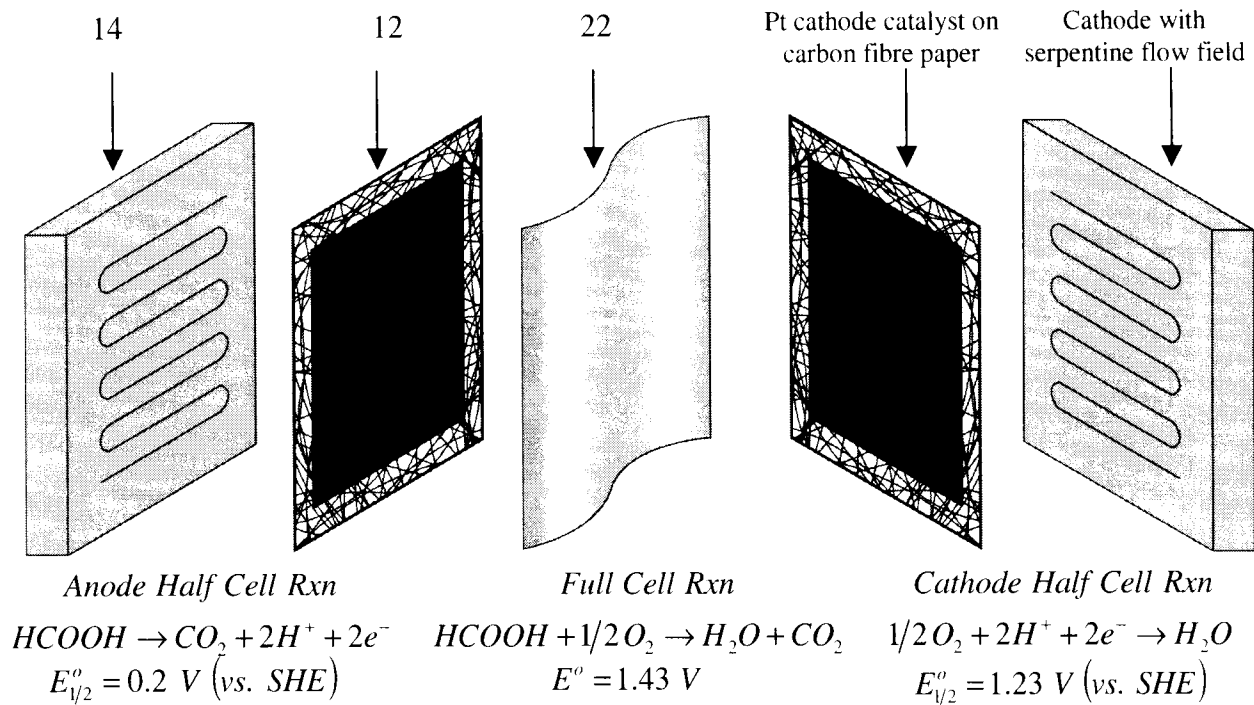


Fig. 4 (Prior Art)

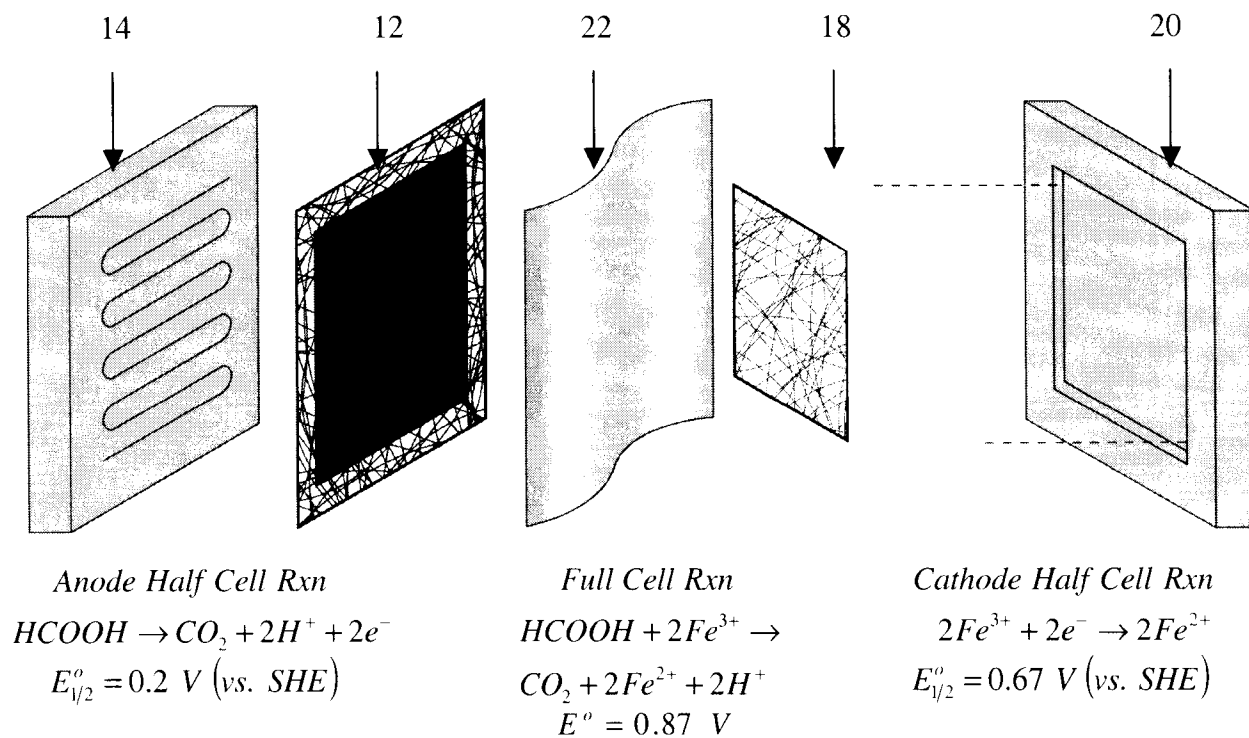
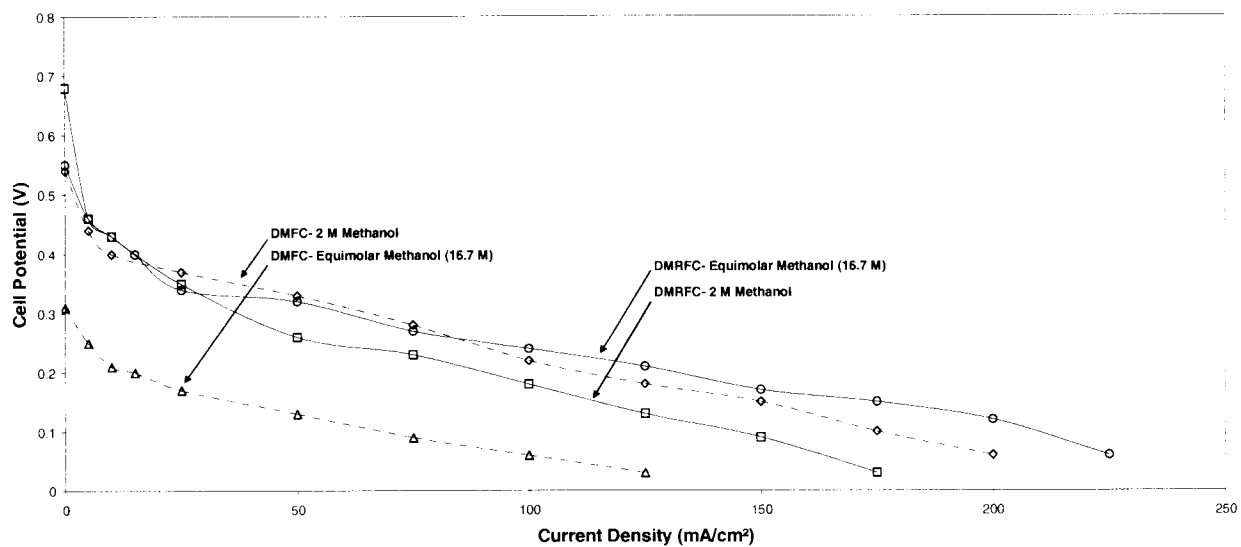
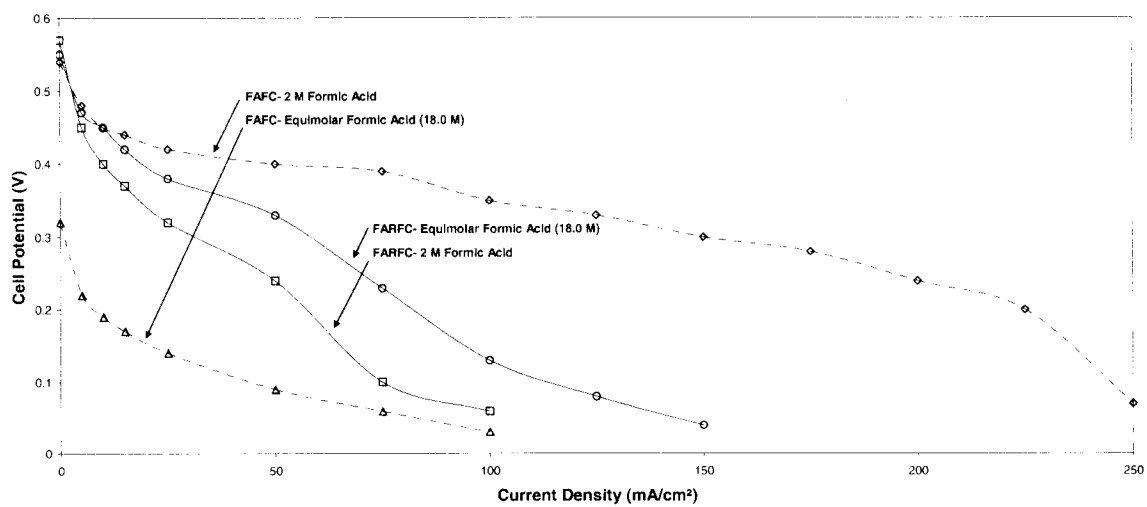
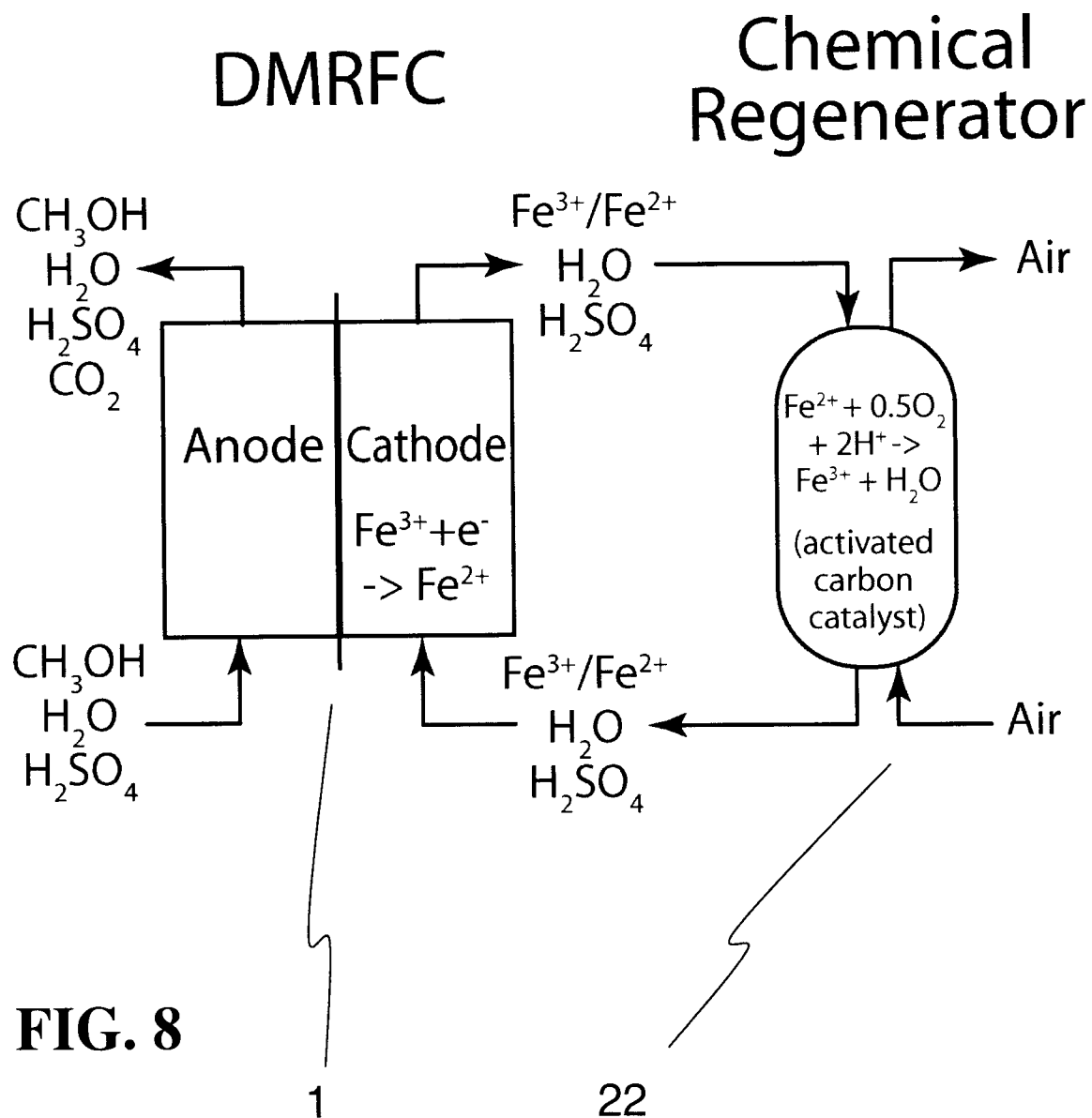


Fig. 5

**Fig. 6****Fig. 7**



INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2008/000732

A. CLASSIFICATION OF SUBJECT MATTER IPC: H01M 8/00 (2006.01) , H01M 4/86 (2006.01) , H01M 8/04 (2006.01) , H01M 8/18 (2006.01) 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) IPC: H01M 8/00 (2006.01) , H01M 4/86 (2006.01) , H01M 8/04 (2006.01) , H01M 8/18 (2006.01) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used) QPAT, Delphion, Derwent, Esp@cenet, CPD, ScienceDirect														
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>P, X P, Y</td> <td>WO 2007/122431 A1 (Creeth et al.) 1 November 2007 (01-11-2007) page 5 lines 12-19 page 6 lines 20-23 page 7 lines 16-24 page 19 lines 1-23 Example 5 Claims 1-10</td> <td>1-5, 8-16 6-7</td> </tr> <tr> <td>Y</td> <td>WO 2006/097438 A2 (Creeth et al.) 21 September 2006 (21-09-2006) page 11 lines 12-15 page 12 line 4- 16 page 4 lines 6-16 page 9 lines 19-20 page 13 lines 7-15 Example 2 Claim 1</td> <td>1-16</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	P, X P, Y	WO 2007/122431 A1 (Creeth et al.) 1 November 2007 (01-11-2007) page 5 lines 12-19 page 6 lines 20-23 page 7 lines 16-24 page 19 lines 1-23 Example 5 Claims 1-10	1-5, 8-16 6-7	Y	WO 2006/097438 A2 (Creeth et al.) 21 September 2006 (21-09-2006) page 11 lines 12-15 page 12 line 4- 16 page 4 lines 6-16 page 9 lines 19-20 page 13 lines 7-15 Example 2 Claim 1	1-16			
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Y	WO 2006/097438 A2 (Creeth et al.) 21 September 2006 (21-09-2006) page 11 lines 12-15 page 12 line 4- 16 page 4 lines 6-16 page 9 lines 19-20 page 13 lines 7-15 Example 2 Claim 1	1-16												
[X] Further documents are listed in the continuation of Box C. [X] See patent family annex. <table border="1"> <tbody> <tr> <td>* Special categories of cited documents :</td> <td>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>"&" document member of the same patent family</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </tbody> </table>			* Special categories of cited documents :	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family	"O" document referring to an oral disclosure, use, exhibition or other means		"P" document published prior to the international filing date but later than the priority date claimed	
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Date of the actual completion of the international search 25 June 2008 (25-06-2008)		Date of mailing of the international search report 24 July 2008 (24-07-2008)												
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476		Authorized officer Laurent de Camprieux 819- 994-0249												

INTERNATIONAL SEARCH REPORT

International application No.
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International application No.
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