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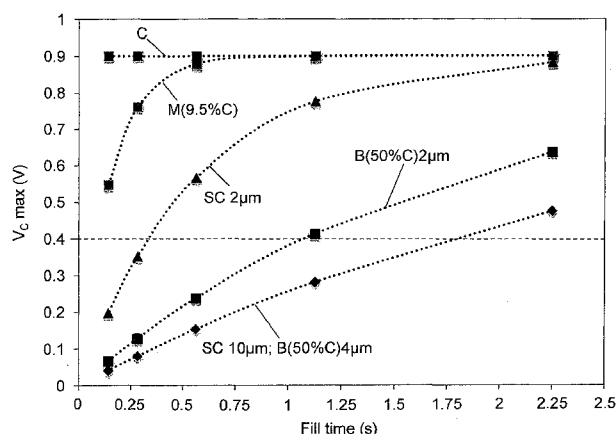


FIG. 4

(57) Abstract: In the development of solid polymer electrolyte fuel cell stacks for commercial purposes, it has been difficult to simultaneously achieve acceptable performance, start-up and shutdown durability, and tolerance to voltage reversal. The present invention resolves this problem by employing an appropriate selectively conducting layer composition in the anode combined with use of a fast hydrogen fill time in the anode components and flow fields during start-ups.

IMPROVED DURABILITY OF FUEL CELL BY USE OF SELECTIVELY CONDUCTING ANODE AND FAST HYDROGEN FILL ON STARTUP

BACKGROUND

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Field of the Invention

The present invention pertains to solid polymer electrolyte fuel cells and particularly to fuel cells intended for automotive applications. Further, the invention pertains to methods and constructions for improving tolerance to voltage reversal while maintaining performance and durability.

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Description of the Related Art

Improving the durability of solid polymer electrolyte fuel cells is one of the challenges preventing the broader commercialization of such fuel cells. A significant problem in this regard is the loss of performance which can be experienced during repeated on-off cycling. During start-up and shutdown events, severe degradation of the carbon supported platinum catalyst which is typically used in such cells can occur. Consequently, such degradation can lead to an unacceptable loss in performance when such fuel cells are subjected to repeated start-up and shutdown cycles. The degradation can be further exacerbated when using low catalyst loadings in the electrodes for cost reduction purposes. Often, there is a trade-off between durability and performance in the fuel cell.

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During the start-up and shutdown of fuel cell systems, various corrosion enhancing events can occur. In particular though, transitions between air and fuel in the anode flow fields are known to cause localized high cathode potentials, thereby resulting in carbon corrosion and platinum dissolution in the cathode catalyst layer. Such temporary high cathode potentials can lead to significant performance degradation. To mitigate this problem, the industry needs to either find more stable and robust catalyst materials or find other means to avoid or slow the associated performance degradation.

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The performance degradation problem due to start-up and shutdown cycling is a key obstacle in the commercialization of solid polymer electrolyte fuel cells. A number of approaches have been suggested in the art for solving this problem, including use of higher catalyst loadings, valves around the stack to prevent air ingress into the anode, and carefully engineered operational start-up and shutdown strategies. Some suggested systems incorporate a nitrogen purge and nitrogen/oxygen purges to prevent damaging gas

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combinations from being present during these transitions (e.g. U.S. Pat. No. 5,013,617 and U.S. Pat. No. 5,045,414).

Some other concepts involve fuel cell stack start-up and shutdown strategies involving fast reactant gas flows to minimize potential spikes. For example, U.S. Pat. No. 6,858,336 and U.S. Pat. No. 6,887,599, disclose disconnecting a fuel cell system from its primary load and rapidly purging the anode with air on shutdown and with hydrogen gas on start-up respectively in order to reduce the degradation that can otherwise occur. While this can eliminate the need to purge with an inert gas, the methods disclosed still involve additional steps in shutdown and start-up that could potentially cause complications. Shutdown and start-up can thus require additional time and extra hardware is needed in order to conduct these procedures.

Still, a more efficient, simple and cost effective method needs to be developed for the industry to overcome the degradation problem. Recently, in PCT patent application serial number WO2011/076396 by the same applicant, it was disclosed that the degradation of a solid polymer fuel cell during start-up and shutdown can be reduced by incorporating a suitable selectively conducting component in electrical series with the anode components in the fuel cell. The component is characterized by a low electrical resistance in the presence of hydrogen or fuel and a high resistance in the presence of air (e.g. more than 100 times lower in the presence of hydrogen than in the presence of air).

It was noted in WO2011/076396 however that the presence of a selectively conducting component or layer could adversely affect a cell's tolerance to voltage reversal along with its performance. It was shown that these adverse effects can be mitigated against in certain ways. For instance, as disclosed in US2014/0030625 by the same applicant, improved voltage reversal results can be obtained by employing a selectively conducting component which comprises a layer of a selectively conducting material and a carbon sublayer in contact with the side of the anode opposite the solid polymer electrolyte. Further, as disclosed in US2015/0325859 by the same applicant, improved voltage reversal results can be obtained by employing a selectively conducting component which comprises a mixed layer comprising a mixture of a selectively conducting material and carbon in contact with the side of the anode opposite the solid polymer electrolyte. The disclosures of WO2011/076396, US2014/0030625, and US2015/0325859 are hereby incorporated by reference in their entirety.

However, improving voltage reversal tolerance using either of the aforementioned approaches can result in a trade-off with regards to the protection obtained against start-up and shutdown degradation. While such a trade-off can be acceptable, it is nonetheless desirable to minimize any trade-off in cell performance, start-

up/shutdown durability, and/or voltage reversal tolerance. The present invention addresses this need and provides other benefits as disclosed below.

SUMMARY

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Use of a selectively conducting layer component in the anode of a solid polymer electrolyte fuel cell desirably improves start-up/shutdown durability. But it has been found to be difficult to simultaneously achieve commercially acceptable voltage reversal tolerance and commercially acceptable performance as well as start-up/shutdown durability in this way. For instance, applying a selectively conducting layer only
10 to a portion or portions of an anode component (i.e. partial coverage of selectively conducting layer) can improve voltage reversal tolerance but at the expense of start-up/shutdown durability. Alternatively, incorporating a carbon sublayer can provide a solution for voltage reversal tolerance, but it can involve a trade-off in performance and/or durability. In yet another alternative, incorporating a mixed layer of a selectively conducting material and carbon material can provide a preferred solution for addressing the
15 voltage reversal tolerance problem. However, in all these approaches, a trade-off still exists between durability and other fuel cell functionalities such as voltage reversal tolerance and performance, and all of these need to be balanced.

The present invention improves on the above and reduces the trade-off that would otherwise be required
20 between these functionalities. The present invention employs an appropriate selectively conducting layer composition in the anode combined with use of a fast hydrogen fill time in the anode components and flow fields during start-up events. Based on actual and modelling results appearing in the Examples below, such an embodiment would be predicted to enjoy the cell performance and voltage reversal tolerance benefits associated with use of the selectively conducting layer composition, while also enjoying substantially
25 improved durability towards the potential degradation associated with start-up events.

Specifically, a fuel cell system of the invention comprises a fuel cell stack comprising a series stack of solid polymer electrolyte fuel cells in which each fuel cell comprises a solid polymer electrolyte, a cathode, anode components, a cathode flow field adjacent the cathode, an anode flow field adjacent the anode components
30 and comprising an inlet and an outlet, and a subsystem for supplying hydrogen to the anode flow fields in the stack. Further, the anode components comprise an anode, an anode gas diffusion layer, and a selectively conducting layer composition. The selectively conducting layer composition comprises a selectively conducting material and a carbon material, and the electrical resistance of the selectively conducting component in the presence of hydrogen is more than 100 times lower than the electrical resistance in the

presence of air. The subsystem for supplying hydrogen is configured to flow an amount of hydrogen equal to the void volume of the anode components and the anode flow fields in a predetermined fill time during start-up of the system. The fuel cell system is characterized in that the resistance of the selectively conducting layer composition in the presence of air and the fill time are selected such that the local cell voltage near the anode outlets is a maximum of 0.4 V over the initial 80% of the fill time during start-up.

In one embodiment, the selectively conducting layer composition comprises a carbon sublayer in contact with the side of the anode opposite the solid polymer electrolyte and a selectively conducting layer comprising the selectively conducting material. In another embodiment, the selectively conducting layer composition comprises a mixed layer in contact with the side of the anode opposite the solid polymer electrolyte wherein the mixed layer comprises a mixture of the selectively conducting material and the carbon material.

In exemplary embodiments, the resistance of the selectively conducting layer in air can be greater than about 0.27 ohms. Further, the predetermined fill time can be in the range from about 0.1 to about 2.5 seconds, and particularly in the range from about 0.1 to about 1.0 seconds. An exemplary subsystem capable of achieving such fill times can comprise a jet pump.

The related method of the invention reduces the degradation during start-up while increasing the tolerance to voltage reversal of an aforementioned fuel cell system and importantly comprises selecting the resistance of the selectively conducting layer composition and the fill time such that the local cell voltage near the anode outlets is a maximum of 0.4 V during start-up.

Being directed to voltage reversal tolerance and performance, the invention is particularly intended for fuel cell stacks and particularly for those in fuel cell systems which will be subjected to numerous start-up and shutdown sequences over the lifetime of the system (e.g. over 10,000) because the accumulated effects of degradation will be much more substantial. For instance, the invention is particularly suitable for automotive applications in which the fuel cell system is the traction power supply for the vehicle and the primary load is the drive system for the vehicle. As discussed in the Examples below, it is expected that the benefits of the invention would be obtained in a relevant fuel cell system which is characterized in that the resistance of the selectively conducting layer composition in the presence of air is less than about 0.1 ohms and the fill time is less than about 50 milliseconds.

The use of a selectively conducting layer composition in a fuel cell anode component, combined with use of relatively fast hydrogen fill times on start-up, provides the advantages of significant protection against start-up stress, system simplification, and cost reduction. Less additional system components are needed, e.g. stack seals, isolation valves, electrical shorting devices, etc. Reductions in catalyst loading may be contemplated since the durability problem can be sufficiently addressed. The use of reactant gases at start-up may be reduced by omitting unnecessary purging, and specialty gases (e.g. nitrogen) are not required.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a schematic illustration of the transient hydrogen gas distribution in an individual solid polymer electrolyte fuel cell along with the local electrochemical reactions potentially taking place therein during start-up.

FIG. 2 compares plots of voltage and current versus time across two illustrative cells in the Examples during simulated start-ups.

FIG. 3 shows a schematic illustration of the equivalent electrical circuit representing the cell of FIG. 1 and which was used to model start-up of several fuel cells in the Examples. FIG. 3a shows the waveform assumed in the modeling.

FIG. 4 shows plots of the maximum local cell voltage near the anode outlet versus H_2 fill times during start-up for fuel cells comprising selectively conducting layer compositions with varied resistance as determined from the modeling in the Examples.

FIG. 5 shows plots of the external cell voltage and the local cell voltages near the anode inlet and outlet versus time during start-up for an actual fuel cell in the Examples.

DETAILED DESCRIPTION

Herein, in a quantitative context, the term “about” should be construed as being in the range up to plus 10% and down to minus 10%.

The term “local cell voltage” refers to the voltage measured between the cathode and anode in the vicinity of (i.e. “near”) a specified point in the fuel cell. More specifically, it is the voltage between the cathode

catalyst and the anode catalyst in the vicinity of (near) the specified point. Thus, any significant voltage drops across components such as gas diffusion layers, flow field plates, and selectively conducting layers are not included in this voltage. Herein, in the context of “local cell voltage”, the term “near” is to be construed according to the dimensions of the actual fuel cell under consideration. Specifically, “near” is to be construed as meaning within a distance equal to 20% of the fuel channel length dimension between the anode inlet and the anode outlet of the actual fuel cell under consideration. As disclosed in the Examples below, local cell voltage can be measured in certain fuel cell stack designs by inserting small electrical leads through the external seals of a fuel cell in the stack so as to contact the relevant components therein (e.g. to contact either side of a catalyst coated membrane or CCM and so as to be located between the CCM and the selectively conducting layer). In alternative but less preferred methods, suitable electrical contacts may have to be included during manufacture or by disassembling and then reassembling the stack with the contacts included.

The degradation associated with start-up and shutdown is one of the most significant degradation problems in solid polymer electrolyte fuel cells. FIG. 1 shows a schematic illustration of the transient hydrogen gas distribution in an individual solid polymer electrolyte fuel cell 1 along with the local electrochemical reactions potentially taking place therein during start-up. In FIG. 1, fuel cell 1 comprises solid polymer membrane electrolyte 2 with anode 3 and cathode 4 adjacent to, but on opposite sides of, membrane electrolyte 2. As shown, fuel cell 1 desirably incorporates porous selectively conducting layer 5 (abbreviated as SOx layer hereinafter) adjacent anode 3. Fuel cell 1 includes gas diffusion layers (GDLs) for each electrode, namely anode GDL 6 adjacent SOx layer 5 and cathode GDL 7 adjacent cathode 4. In addition, fuel cell 1 comprises fuel flow field plate 8 adjacent anode GDL 6 for distributing fuel to anode 5 and oxidant flow field plate 9 for distributing air oxidant to cathode 4. Anode inlet 10 and anode outlet 11 are also shown in FIG. 1 but to avoid clutter, other features of a typical fuel cell have been omitted.

Prior to start-up, the anodes and fuel flow fields in such fuel cells can be filled with air, either deliberately for storage purposes or as a result of leakage. During a start-up event, H₂ fuel is supplied to the anode inlet 10 of fuel cell 1 and moves through the fuel flow fields in fuel flow field plate 8, displacing air and creating a H₂ - Air front (indicated by dashed line 12 in FIG. 1) which is initially near anode inlet 10. The presence of this H₂ - Air gas front 12 effectively creates a shorted cell between that portion of the cell near the anode outlet 11 (where air is still present) and that portion of the cell near anode inlet 10 (where hydrogen is present). The associated current 13 flows through all the electrically conductive components between these two portions. However, due to the nature of the material properties and dimensions involved, this current mainly flows through the lower resistance fuel flow field plate 8 which is typically used in such cells (as

suggested by current arrow 13 in FIG. 1). This transient situation causes loop currents to flow within the cell as illustrated by the current flowing primarily from anode inlet 10 to anode outlet 11 in fuel flow field plate 8 and the current 14 flowing in the opposite direction in oxidant flow field plate 9 in FIG. 1. Completing the effective current loop are protons which also flow locally in opposing directions across membrane electrolyte 2 as indicated by arrows 15, 16 in FIG. 1. As start-up continues, H₂ - Air gas front 12 steadily moves towards anode outlet 11 (i.e. to the right in FIG. 1) as hydrogen fuel displaces air to fill the voids in anode 3, SO_x layer 5, anode GDL 6, and fuel flow field plate 6. The loop current situation illustrated in FIG. 1 still exists though until hydrogen has completely filled the anode spaces at which point H₂ - Air gas front 12 no longer exists and this transient situation has ended.

Such loop currents can result in significant degradation to the cathode catalyst layer near the anode outlet because the potential of the cathode can be temporarily driven well above normal relative to the standard hydrogen electrode (SHE). For instance, at cathode potentials above about 1.2 V versus SHE, significant corrosion of the cathode components can occur. Because hydrogen is present at anode 3 in the vicinity of anode inlet 10, locally here the fuel cell is capable of producing power and this provides the electromotive force behind loop currents 13, 14. However, with air present at anode 3 in the vicinity of anode outlet 11, the anode catalyst in this vicinity temporarily behaves as a typical cathode instead. In a conventional fuel cell with air initially present at both the cathode and anode, an estimate of the anode potential versus SHE in the vicinity of the anode outlet during start-up is about 0.8 V. (This estimate is based on empirically observing current densities of about 0.1-0.2 A/cm² during start-up/shutdown events and correlating that to known voltage versus current density characteristics for such a fuel cell.) The local cell voltage near anode inlet 10 (i.e. the voltage between cathode and anode here) would also similarly be about 0.8 V. And because the flow field plates are such relatively good conductors, this voltage difference is essentially imposed across cathode 4 and anode 3 in the vicinity of anode outlet 11. Consequently, the cathode potential versus SHE in the vicinity of anode outlet 11 can be about 0.8 + 0.8 V or about 1.6 V versus SHE. At such potentials, the cathode materials are subject to severe degradation.

The electrochemical reactions which can occur as a result of this situation where both hydrogen and air reactants exist in the anode are illustrated in FIG. 1. As discussed above, H₂ - Air front 12 causes the anode inlet and anode outlet ends of the fuel cell to behave as independent cells connected in series. The anode inlet side of the cell acts as a power supply, pushing current backwards through the anode outlet side of the cell. As shown in FIG. 1, numerous undesirable reactions can occur which lead to the degradation of various cell components. However, these reactions require electron flow in order to take place and thus preventing loop currents 13, 14 can prevent degradation in principle.

As discussed above, this degradation can thus be reduced via the incorporation of a suitable selectively conducting component in electrical series with the anode components in the fuel cell in accordance with the teachings in WO2011/076396 (for instance, SOx layer 5 located between anode 3 and anode GDL 6).

5 The component is characterized by a low electrical resistance in the presence of hydrogen or fuel and a high resistance in the presence of air (e.g. more than 100 times lower in the presence of hydrogen than in the presence of air). However, the presence of a selectively conducting component or layer can adversely affect the fuel cell's tolerance to voltage reversal along with its performance. In order to mitigate against these adverse effects, an appropriate carbon sublayer may also be incorporated (i.e. in contact with the side of the
10 anode opposite the solid polymer electrolyte as disclosed in US2014/0030625). Alternatively, an amount of carbon material may instead be mixed in with the selectively conducting material itself to make a mixed layer which can be used as the selectively conducting component (as disclosed in US2015/0325859). Although these approaches improve voltage reversal tolerance and cell performance, a trade-off is required with regards to protection against start-up degradation.

15 The present invention can overcome this trade-off in protection against start-up degradation. Superior start-up and shutdown protection can be provided while still providing acceptable voltage reversal tolerance and cell performance. Fuel cell systems of the invention comprise a fuel cell stack made of a series stack of solid polymer electrolyte fuel cells, each comprising anode components including a selectively conducting
20 layer composition. The selectively conducting composition comprises a suitable selecting conducting material (e.g. a tin oxide, platinum deposited on tin oxide, etc.) and a carbon material. The carbon material can be present in the form of a sublayer in contact with the side of the anode opposite the solid polymer electrolyte. Alternatively, the carbon material can be mixed with the selectively conducting material and used as a mixed layer in contact with the side of the anode opposite the solid polymer electrolyte. The use
25 of the selectively conducting layer composition provides for improved durability on start-up and shutdown, while the presence of the carbon sublayer or mixed carbon layer mitigates against associated losses in voltage reversal tolerance and also cell performance.

In addition though, fuel cell systems of the invention comprise a subsystem configured to quickly supply
30 hydrogen to the anode flow fields during start-up. Use of a suitably fast hydrogen fill time on start-up overcomes the trade-off in start-up protection associated with embodiments comprising the aforementioned carbon sublayer or the mixed layer of carbon and selectively conductive material.

The hydrogen fill time for a fuel cell stack is essentially equal to the time it takes to flow an amount of hydrogen equal to the void volume of the anode components therein. The subsystem is thus configured to flow this amount of hydrogen in a predetermined time, i.e. a predetermined fill time.

- 5 The void volume of the anode components in a cell can readily be measured experimentally. For instance, the anode side of the cell can be pressurized with a test gas at an accurately known pressure and then allowed to equilibrate with reference gas of accurately known volume and a different but accurately known pressure, all at constant temperature. From the measured pressure of the equilibrated mixture, the volume of the anode components can be calculated. Alternatively, the void volume of the anode components in a cell can
10 be calculated reasonably well based on a knowledge of the cell design and the dimensions, porosities, masses, densities, etc. of the various components therein.

- The volume of gas which flows through the cell during the transient conditions experienced during start-up can be hard to determine accurately based on time and flow rate measurements alone (due to changes
15 experienced in gas composition, pressure, and temperature in this transient period). However it is readily possible to measure the volume which has flowed through the cell by measuring the volume of the gas exhausted from the cell anode at a given temperature and pressure.

- Generally, the component which is the most susceptible to degradation in the fuel cell on start-up is the
20 cathode in the vicinity of the anode outlets. Thus, preventing the cathode potential here from exceeding an unacceptable value during start-up (e.g. about 1.2 volts versus SHE) should prevent degradation throughout the fuel cell on start-up. And, as above, if the anode potential versus SHE when air is present here during start-up is about 0.8 V, then keeping the local cell voltage (i.e. the voltage between cathode and anode electrode layers here) below about 0.4 V should therefore successfully prevent degradation throughout. As
25 illustrated from modeling done in the Examples below, it should be possible to do this by using a selectively conducting layer composition with appropriate resistance characteristics in combination with using an appropriately fast hydrogen fill time. It is then possible to reduce the loop current and the local cell voltage near the anode outlets such that degradation conditions are avoided. However, as hydrogen replaces the air present in the anode in the vicinity of the anode outlets during start-up, the local anode potential versus
30 SHE there drops and the local cell voltage can and should be allowed to rise to normal values without resulting in corrosion of the cathode components.

Given the preceding definitions then, over the initial 80% of the fill time, the H₂ - Air gas front 12 has essentially moved over 80% of the distance along the fuel channel length dimension between the anode

inlet and the anode outlet and thus has not yet moved into the region “near” the anode outlets (which by definition is the region within 20% of the anode outlets). In accordance with the invention then, the local cell voltage near the anode outlets is kept to a maximum of 0.4 V over the initial 80% of the fill time. However over the last 20% of the fill time, the H₂ - Air gas front 12 moves through the region near the anode outlets, replacing the air here with hydrogen.

Using these principles, and within certain limits, fuel cell systems with superior start-up and shutdown protection can be obtained while acceptably meeting all other performance criteria. With a suitable predetermined fill time, the current design space for acceptable selectively conducting layer compositions can be widened. For instance, it is expected that commercially acceptable fuel cell systems can employ selectively conducting layer compositions with resistances in air ranging up to at least about 0.27 ohms. Further, it is expected that predetermined fill times less than about 2.5 seconds can be suitable, and more preferably less than about 1.0 seconds. On the other hand however, based on estimates discussed in the Examples below, it is expected that commercially acceptable automotive fuel cell systems might employ selectively conducting layer compositions with resistances in air of about 0.1 ohms or less but with predetermined fill times of about 50 milliseconds or less. Systems equipped with jet pumps for the hydrogen fuel are, for instance, capable of providing sufficient flow rates to achieve such fast fill times.

The following Examples have been included to illustrate certain aspects of the invention but should not be construed as limiting in any way.

EXAMPLES

Illustrative simulated start-ups of fuel cells

To investigate the magnitudes of the initial transient voltages and currents experienced in fuel cells under typical start-ups, a conventional fuel cell with no selectively conducting anode layer and a fuel cell comprising a 10 μ m relatively thick selectively conducting layer (with no added carbon material) were assembled and subjected to simulated start-up conditions. The active area in both cells was about 50 cm².

Specifically, the fuel cells were tested in a state which is typical of start-ups, namely with air present over both the anode and cathode sides of the cell and at ambient room temperature and relative humidity conditions. During testing, no reactant flow was provided to either anode or cathode. A power supply was

connected across each tested fuel cell and a fast transient voltage ramp was applied. While the voltage ramp was applied, the current and voltage seen across the cell was continuously monitored. The voltage ramp consisted of a linear ramp from 0 to 1 volt over a period of 0.1 seconds. These conditions were intended to roughly simulate those experienced within a fuel cell in the situation depicted in FIG. 1. In particular, the voltage applied by the power supply attempts to simulate the portion of the fuel cell near anode inlet 10 where the cell first starts becoming active and generating power as hydrogen enters the anode side of the cell. The voltage and current measured across the cell is indicative of values experienced over the portion of the fuel cell near anode outlet 11.

FIG. 2 compares the plots of measured voltage and current across these fuel cells versus time during such simulated start-up events. (The conventional cell and the cell with the selectively conducting layer are denoted as “conventional” and “SOx” in FIG. 2 respectively.) In the conventional cell, a current density as high as 3.0 A/cm^2 was seen which would be expected to cause significant damage to the cathode catalyst layer in the fuel cell over repeated start-ups. On the other hand, in the SOx cell, there was essentially no current seen (e.g. no loop current like that depicted in FIG. 1). [Note that the voltage spike seen across the SOx cell is believed to be an artefact arising from limitations in the capability of the power supply used in this testing.]

This example demonstrates the potential for damage in conventional cells on start-up, but also the potential for avoiding damage using selectively conducting layer technology. Further, the results suggest that cell behaviour in this regard may be successfully modeled using simple analogous electric circuits.

Modeling of local cell voltage near anode outlets

Here, the start-up event situation depicted in FIG. 1 was modeled using a simple equivalent electrical circuit and characteristics for the various components obtained from actual representative fuel cell components.

The equivalent circuit used in this modeling is shown in the schematic illustration of FIG. 3. In this simple resistor-capacitor (RC) circuit, power supply V represents the active inlet portion of the fuel cell (i.e. the combination of anode 3, electrolyte 2, and cathode 4 in the vicinity of anode inlet 10 which together act as a power supply when both hydrogen and air are present as shown in FIG. 1), capacitor C represents the inactive outlet portion of the fuel cell (i.e. the combination of anode 3, electrolyte 2, and cathode 4 in the vicinity of anode outlet 11 which act as a capacitor in this circuit when air is present on both electrodes as shown in FIG. 1), and R represents the resistance of SOx layer 5 plus that of anode GDL 6 in air. (The

resistances of the other fuel cell components were not included for simplicity since their values are so relatively low. When a selectively conducting layer like SOx layer 5 is present, its resistance in air is generally the dominant resistance in this model.) The voltage signal provided by power supply V is thus the local cell voltage (i.e. between cathode and anode) near anode inlet 10. The voltage across C is thus the local cell voltage near anode outlet 11. The voltage across R is the voltage drop across SOx layer 5 and anode GDL 6.

To simulate a typical start-up event, a signal with the characteristic waveform shown in FIG. 3a was provided by power supply V to the RC circuit. As shown, the signal starts at 0 V, ramps up linearly to 1 V over a time period equal to $1/5 \times$ “fill time”, remains at a constant 1 V over a time period equal to $4/5 \times$ “fill time”, and then ramps down linearly again to 0 V at the same ramp rate as before. The initial 0 V signal simulates conditions at the beginning of a start-up event where both anode and cathode sides of the fuel cell are assumed to be filled with air. The ramp up period is intended to simulate the time period where the portion of the fuel cell near anode inlet 10 first fills with hydrogen. The inlet portion of the fuel cell is becoming active and the end of the ramp period represents that point when the anode inlet is essentially just filled with hydrogen. Next, the constant 1 V time period represents the situation as H₂ - Air front 12 moves steadily towards anode outlet 11 (the 1 V level being selected for convenience). Where the signal voltage starts to decrease again represents the point at which the anode components are considered to have essentially become filled with hydrogen (assumed to be the “fill time” in the model). The selection of a ramp time of $1/5 \times$ “fill time” was based on empirical current mapping results made in a test cell which suggested that the local cell voltage near the anode inlet rose to about 1 V after about 20% of the anode flow field filled with hydrogen.

Capacitor C represents the portion of the cell near the anode outlet and this is where the cathode catalyst layer experiences the highest cathode overpotential during start-ups. In order to prevent degradation of the fuel cell components (e.g. cathode carbon components), the cathode overpotential should remain below about 1.2 V versus SHE. As discussed above, since the anode potential versus SHE in this portion of the cell during start-up is about 0.8 V, in order to prevent degradation then, the voltage across C is desirably kept below about 0.4 V in this model.

With this simple model then, the transient behavior in fuel cells was predicted for various selectively conducting layer designs. In the following, a capacitance of 6 farads was assumed for capacitor C, which is a typical value for catalyst coated membranes (CCMs) intended for automotive applications. As described in more detail below, several actual fuel cells with anodes comprising selectively conducting

layer compositions of varied design were made, along with a comparative fuel cell with no such layer. The total resistances of these selectively conducting layers and adjacent anode GDLs were determined by fitting experimental data obtained on actual cell assemblies as explained in more detail below. These resistances were used in the model as different values for resistor R. And finally, using these values for C and R in the equivalent circuit of FIG. 3, the maximum voltage V_C which would be seen across capacitor C was calculated as a function of fill time (i.e. ramp time from 0 to 1 V).

Six different anode designs were considered in the modeling. These anode designs had previously been used in actual experimental fuel cells whose performance, voltage reversal, and start-up/shutdown durability characteristics had previously been determined. Three of these cells contained selectively conducting layer compositions which included carbon material, two cells contained selectively conducting layers with no carbon material included, and one cell contained no selectively conducting layer.

The cells all comprised CCMs sandwiched between anode and cathode gas diffusion layers (GDLs) comprising commercial carbon paper from Freudenberg. The CCMs all had membrane electrolytes made of 18 micrometer thick perfluorosulfonic acid ionomer which had been coated on opposite sides with the desired anode and cathode catalyst layers. The catalyst used in the conventional carbon supported platinum (Pt/C) cathode and anode catalyst layers was a commercial product comprising about 46% Pt by weight. The coated catalyst layer in the cathodes and anodes comprised about 0.4 and 0.1 mg/cm² of Pt respectively.

Where applicable, the selectively conducting layers and mixed layers used in the cells comprised of SnO₂ (obtained from SkySpring Nanomaterials Inc. and characterized by particle sizes between 50 and 70 nanometers and a surface area between 10 and 30 m²/g). The mixed layers also comprised varied amounts of synthetic graphite (KS4 from Timcal). Selectively conducting oxide layers (SO_x layers) were incorporated as coatings on a side of the anode GDLs. The coatings were applied using a solid – liquid ink dispersion comprising a mixture of the SnO₂, METHOCELTM methylcellulose polymer, distilled water, and isopropyl alcohol. PTFE was included as a binder in the dispersions. The dispersions were then applied, dried, and sintered as described in the aforementioned PCT patent application WO2011/076396. The thickness of a single application of a selectively conducting anode layer was in the range from about 10 – 15 micrometers.

Assemblies comprising the appropriate CCMs, SO_x layer, and anode and cathode GDLs were then bonded together under elevated temperature and pressure and placed between appropriate cathode and anode flow field plates to complete the experimental fuel cell constructions. The resistance of each of the anode

components was then determined by performing similar testing on these fuel cells as described above with regards to FIG. 2 (namely by measuring the current and cell voltage responses to the applied voltage ramp) and then fitting those sets of responses to the RC model proposed in FIG. 3. Table 1 summarizes the different compositions used in the anode components along with the resistances of each for these six experimental fuel cells.

Performance and reversal tolerance characteristics were determined in the following manner. Cells were first conditioned by operating at a current density of 1.5 A/cm^2 , with hydrogen and air as the supplied reactants at 100 %RH, and at a temperature of 60°C for at least 16 hours to obtain a stable steady-state performance. Performance characteristics were determined by measuring output voltage as a function of current density applied otherwise under the same conditions as above. The voltage at a current density of 1.5 A/cm^2 was measured and is tabulated in Table 1.

Voltage reversal testing involved operating the cells first at a lower current density of 1.0 A/cm^2 for 2 hours, then turning off the current, switching the reactant supply to the anode from hydrogen to nitrogen instead, and then forcing 0.2 A/cm^2 from the cell thereby subjecting the cells to voltage reversal conditions. Typically, the cell voltage would roughly plateau at a value between 0 and about -3 V for a variable amount of time and then drop off suddenly to a value much less than -5 V , at which point testing ended. The length of time to this sudden drop off point is representative of the cell's ability to tolerate voltage reversal and is denoted in Table 1 as the reversal time.

To evaluate start-up/shutdown durability, the cells were operated at a current density of 1.5 A/cm^2 using hydrogen and air reactants at 70°C and 100 %RH and were periodically subjected to start-up/shutdown cycles designed to accelerate degradation. The cycling comprised removing the electrical load while maintaining the flow of reactants for 10 seconds, stopping flow of air and allowing hydrogen to diffuse from anode to cathode for 150 seconds, purging both cathode and anode with air in aligned air-air front fashion across the flow fields, removing both reactant flows and allowing air to diffuse from cathode to anode for 30 seconds, flowing hydrogen on anode and air on cathode while ramping the load to draw 1.5 A/cm^2 for 300 seconds, and repeating. The hydrogen fill time in this testing was approximately 0.5 to 0.6 seconds. The voltage output of each cell was recorded after each start-up/shutdown cycle. In addition, polarization characteristics (i.e. voltage as a function of current density) were obtained for the cells throughout the start-up/shutdown cycle testing. From this, a performance degradation rate was calculated in units of μV per cell per start-up/shutdown cycle. The relative improvement compared to comparative cell C, referred to herein as the durability improvement factor, is also tabulated in Table 1.

Table 1.

Cell #	Selectively conducting anode component	Resistance of anode components (ohms, in air)	Reversal time (min)	Output voltage @ 1.5 A/cm ² (V)	Durability improvement factor
C	None; conventional comparative cell	0.002	77	0.649	not applicable
SC 2μm*	Selectively conducting layer only; thickness 2 microns; comparative cell	0.085	75	0.642	-
SC 10μm	Selectively conducting layer only; thickness 10 microns; comparative cell	0.45	0.33	0.596	4.0x
M(9.5%C)	Mixed layer with 9.5% KS4 by weight; thickness 6 microns	0.0225	61	0.632	not available
B(50%C)2μ	Bilayer construction; mixed layer with 50% KS4 by weight, thickness 3 microns; & selectively conducting layer, thickness 2 microns	0.275	71	0.643	2.2x
B(50%C)4μ	Bilayer construction; mixed layer with 50% KS4 by weight, thickness 2 microns; & selectively conducting layer, thickness 4 microns	0.45	71	0.651	2.5x

*Cell # SC 2 μ m had similar but not exactly the same construction as the other cells in the series and so rigorous quantitative comparison is not appropriate here.

As is evident from the data in Table 1, the presence of the selectively conducting layer provides a marked improvement in start-up/shutdown durability. However, performance and, in particular, voltage reversal characteristics can be adversely affected. By additionally using either carbon sublayers or mixed layers though, the loss in performance and voltage reversal tolerance can be avoided but with a trade-off in start-up/shutdown durability.

Using the resistances from the various actual anode components from Table 1 and the aforementioned model, FIG. 4 plots of the maximum V_C (equivalent to local cell voltage near the anode outlet) versus H_2 fill times during start-up for these fuel cells. As is apparent from FIG. 4, for H_2 fill times greater than about 2.5 seconds, most of the experimental fuel cells would be expected to have maximum V_C voltages that exceed 0.4 V and hence would be expected to experience degradation on start-up. Somewhat surprisingly, the maximum V_C for the conventional comparative cell C remains well above 0.4 V for fill times below even 0.25 seconds. Since it is generally not practical to achieve hydrogen fill times much below this value, it would not seem practically possible to avoid degradation conditions in such conventional cells on start-up. However, as the resistance of the anode design increased, the maximum V_C is seen to decrease significantly with faster hydrogen fill times. The comparative SC 2 μ m cell for instance showed a maximum V_C below 0.4 V for fill times less than about 0.3 seconds. And the three cells SC 10 μ m, B(50%C)2 μ , and B(50%C)4 μ all showed a maximum V_C below 0.4 V for fill times less than about 1.0 seconds.

The modeling results in FIG. 4 show that desirable conditions for preventing degradation on start-up can be expected using actual anode compositions comprising selectively conducting layers with sufficiently low, but still practically possible, hydrogen fill times (e.g. between about 0.25 and 2.5 seconds). These anode compositions include embodiments whose selectively conducting layer comprises a carbon mixture. As demonstrated previously, use of such anode compositions can also be expected to provide acceptable voltage reversal tolerance and cell performance. In addition, FIG. 4 shows that with today's typical high performance fuel cell designs, conventional fuel cells may be unable to avoid degradation conditions on start-up. Further, FIG. 4 provides guidance with regards to the potential for various selectively conducting layer designs to be employed in fuel cell systems while still meeting specific durability and functional requirements.

Start-up of actual instrumented fuel cell

An experiment was designed and carried out to measure the local cell voltage in a typical fuel cell during start-up. The active area of the cell was 10 cm long by 4 cm wide. The cell employed a typical catalyst coated membrane (CCM), with gas diffusion layers (GDLs) on each side thereof, and with flow field plates comprising straight channels adjacent each GDL. In addition, a thick, pure selectively conducting layer was employed between the anode GDL and the anode side of the CCM. The resistance of the selectively conducting layer was 1 ohm in the presence of air. In order to measure the local cell voltage, small voltage pickup leads were carefully inserted from outside the fuel cell and through the cell seals, perpendicular to the active area, so as to appropriately contact the anode and cathode catalyst layers of the CCM. In the case of the anode contact, voltage pickup leads were placed between the anode side of the CCM and the selectively conducting layer. For the cathode contact, voltage pickup leads were placed between the cathode side of the CCM and a cathode diffusion layer in the cell. In this experiment, the local cell voltages near the anode inlet and also near the anode outlet were measured. Specifically, the location of the anode inlet leads were 10 mm from the start of the active area, while the anode outlet leads were located at 85 mm from the start of the active area. When operating, the reactant flow configuration was co-current flow with air and hydrogen fuel being used as the reactants.

The cell was initially operated to condition the MEA. Then, air was purged through the anode to create an air/air state on the cathode/anode sides of the cell. The cell then underwent a start-up in which hydrogen was introduced and flowed into the anode while air was present at the cathode. During this start-up, the external cell voltage, the local cell voltage near the anode inlet, and the local cell voltage near the anode outlet were all measured and recorded by oscilloscope. Figure 5 shows plots of all these voltages versus time.

As can be seen by comparing the external cell voltage in Figure 5 to the local cell voltages, both the local cell voltage near the anode inlet and near the anode outlet rise with a significant time lag during start-up. The anode void volumes were not determined for this example, but the fill time was estimated from the observed external cell voltage behaviour. That is, the initial rise in the external cell voltage was assumed to be the time when hydrogen enters or starts to fill the active area of the cell. And the time at which the external cell voltage stops rising and levels off was assumed to be when hydrogen has essentially reached the anode outlet of the cell. The difference between these times is an estimate of the fill time, and in the Example shown in Figure 5, the fill time is estimated to be approximately 0.25 seconds.

As is evident from Figure 5, the local cell voltage near the anode inlet rises much more quickly than the local cell voltage near the anode outlet. After the initial 0.2 seconds, or about 80% of the 0.25 second fill time, the local cell voltage near the anode inlet has greatly exceeded 0.4 V (e.g. 0.7+ V). However, after the same initial 0.2 seconds, where air is still expected to remain at the anode outlet, the local cell voltage near the anode outlet is still observed to be less than 0.4 V. Thus, the corrosion reactions shown in Figure 1 near the anode outlet are avoided.

This Example demonstrates how the local cell voltages near the anode inlets and outlets can be measured and how they can vary when employing a suitable selectively conducting layer in a cell coupled with a suitably fast fill time. In particular, it demonstrates that corrosive conditions at the cathode near the anode outlet can be avoided.

Estimates of required resistance and fill times for automotive fuel cell stacks

In this Example, estimates were made of the required resistance of a selectively conducting layer and of the required fill time for purposes of using the invention in typical automotive fuel cell stacks.

The required fill time for preventing the local cell voltage near the anode outlet from rising above 0.4 V during start-up is primarily influenced by the resistance of the selectively conducting layer and the capacitance properties of the CCM used in the fuel cells. Using the electrical circuit model of Figure 3 and assuming a transient voltage change from 0 V to 1 V, the rise time to 0.4 V can be calculated as a function of capacitance and resistance. Using fill times that are faster than what the model predicts for the time taken to reach 0.4 V are expected to ensure that the voltages across the CCM do not exceed 0.4 V where there is a transient air/air environment in the cell during start-up.

For a range of expected CCM capacitance values of from 0.1 to 10 Farad and resistances for the selectively conducting layers of from 0.01 ohms to 5 ohms, the maximum fill time based on the model in Figure 3 has been determined to be $t_{MAX} = 0.5 * R_{SOX} * C_{CCM}$, where R_{SOX} is the resistance of the selectively conducting layer in air in ohms for the whole cell and where C_{CCM} is the capacitance for the whole cell in farads. The capacitance of the CCM in a fuel cell depends on the size of the active area and the composition of the layers. For instance, doubling the size of the active area of the same CCM type will essentially double the cell capacitance. Depending on the fuel cell application, active areas can vary greatly.

As reasonable estimates for typical present day automotive fuel cells, the resistance of the selectively conducting layer in air is expected to be less than about 0.1 ohms and the CCM capacitance is expected to be about 1 farad. Using these estimates, a maximum fill time of 50 milliseconds would be required then based on the equation above. Thus, automotive type fuel cell stacks might be expected to enjoy the benefits if the invention if they include a selectively conducting layer with resistances in air of about 0.1 ohms or less and when employing fill times on start-up of less than about 50 milliseconds.

The preceding examples show that cells or stacks comprising a mixed layer of selectively conducting material and carbon material can be engineered to avoid undesirable local cell voltages near the anode outlets during start-up and that they would be expected to have markedly improved start-up performance using faster hydrogen fill times. Since use of faster fill times is not expected to adversely affect voltage reversal tolerance or cell performance, such cells or stacks would be expected to be completely acceptable in all these regards.

All of the above U.S. patents, U.S. patent application publications, U.S. patent applications, foreign patents, foreign patent applications and non-patent publications referred to in this specification, are incorporated herein by reference in their entirety.

While particular elements, embodiments and applications of the present invention have been shown and described, it will be understood, of course, that the invention is not limited thereto since modifications may be made by those skilled in the art without departing from the spirit and scope of the present disclosure, particularly in light of the foregoing teachings. Such modifications are to be considered within the purview and scope of the claims appended hereto.

WHAT IS CLAIMED IS:

1. A fuel cell system comprising:

a fuel cell stack comprising a series stack of solid polymer electrolyte fuel cells wherein each fuel cell comprises a solid polymer electrolyte, a cathode, anode components, a cathode flow field adjacent the cathode, and an anode flow field adjacent the anode components and comprising an inlet and an outlet wherein:

i) the anode components comprise an anode, an anode gas diffusion layer, and a selectively conducting layer composition;

ii) the selectively conducting layer composition comprises a selectively conducting material and a carbon material; and

iii) the electrical resistance of the selectively conducting component in the presence of hydrogen is more than 100 times lower than the electrical resistance in the presence of air; and

a subsystem for supplying hydrogen to the anode flow fields in the stack wherein the subsystem is configured to flow an amount of hydrogen equal to the void volume of the anode components and the anode flow fields in a predetermined fill time during start-up of the system;

characterized in that the resistance of the selectively conducting layer composition in the presence of air and the fill time are selected such that the local cell voltage near the anode outlets is a maximum of 0.4 V over the initial 80% of the fill time during start-up.

2. The fuel cell system of claim 1 wherein the selectively conducting layer composition comprises a carbon sublayer in contact with the side of the anode opposite the solid polymer electrolyte and a selectively conducting layer comprising the selectively conducting material.

3. The fuel cell system of claim 1 wherein the selectively conducting layer composition comprises a mixed layer in contact with the side of the anode opposite the solid polymer electrolyte wherein the mixed layer comprises a mixture of the selectively conducting material and the carbon material.

4. The fuel cell system of claim 1 wherein the resistance of the selectively conducting layer in air is greater than about 0.27 ohms.

5. The fuel cell system of claim 1 wherein the predetermined fill time is in the range from about 0.1 to about 2.5 seconds.

6. The fuel cell system of claim 5 wherein the predetermined fill time is in the range from about 0.1 to about 1.0 seconds.

7. The fuel cell system of claim 1 wherein subsystem for supplying hydrogen to the anode flow fields in the stack comprises a jet pump.

8. A fuel cell system comprising:

a fuel cell stack comprising a series stack of solid polymer electrolyte fuel cells wherein each fuel cell comprises a solid polymer electrolyte, a cathode, anode components, a cathode flow field adjacent the cathode, and an anode flow field adjacent the anode components and comprising an inlet and an outlet wherein:

i) the anode components comprise an anode, an anode gas diffusion layer, and a selectively conducting layer composition;

ii) the selectively conducting layer composition comprises a selectively conducting material and a carbon material; and

iii) the electrical resistance of the selectively conducting component in the presence of hydrogen is more than 100 times lower than the electrical resistance in the presence of air; and

a subsystem for supplying hydrogen to the anode flow fields in the stack wherein the subsystem is configured to flow an amount of hydrogen equal to the void volume of the anode components and the anode flow fields in a predetermined fill time during start-up of the system;

characterized in that the resistance of the selectively conducting layer composition in the presence of air is less than about 0.1 ohms and the fill time is less than about 50 milliseconds.

9. A method for reducing the degradation during start-up and for increasing the tolerance to voltage reversal of a solid polymer electrolyte fuel cell stack in a fuel cell system, the fuel cell stack comprising a series stack of solid polymer electrolyte fuel cells wherein each fuel cell comprises a solid polymer electrolyte, a cathode, anode components, a cathode flow field adjacent the cathode, and an anode flow field adjacent the anode components and comprising an inlet and an outlet, the method comprising:

obtaining anode components comprising an anode, an anode gas diffusion layer, and a selectively conducting layer composition wherein the selectively conducting layer composition comprises a selectively conducting material and a carbon material; and the electrical resistance

of the selectively conducting component in the presence of hydrogen is more than 100 times lower than the electrical resistance in the presence of air;

providing a subsystem for supplying hydrogen to the anode flow fields in the stack wherein the subsystem is configured to flow an amount of hydrogen equal to the void volume of the anode components and the anode flow fields in a predetermined fill time during start-up of the system; and

selecting the resistance of the selectively conducting layer composition in the presence of air and the fill time such that the local cell voltage near the anode outlets is a maximum of 0.4 V over the initial 80% of the fill time during start-up.

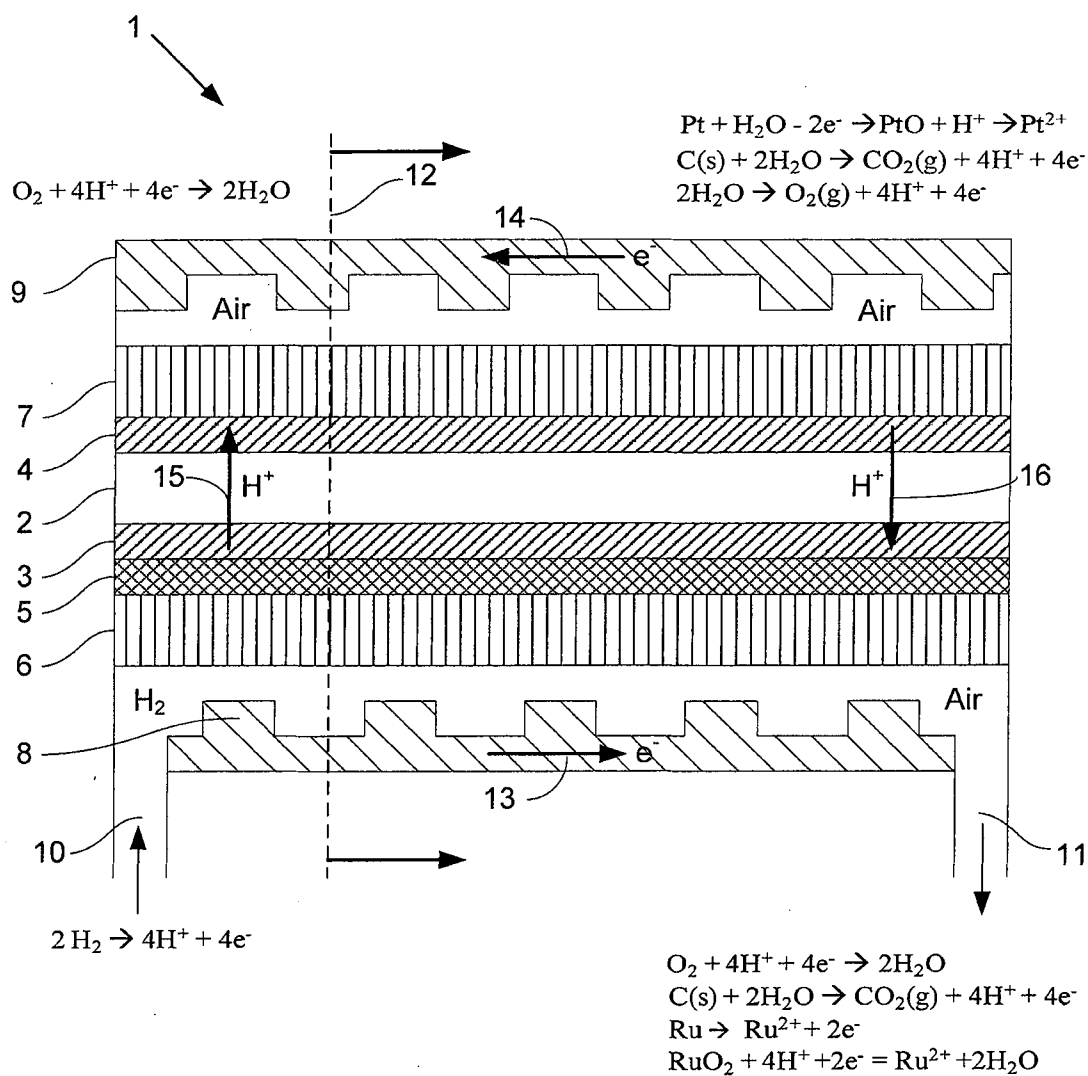
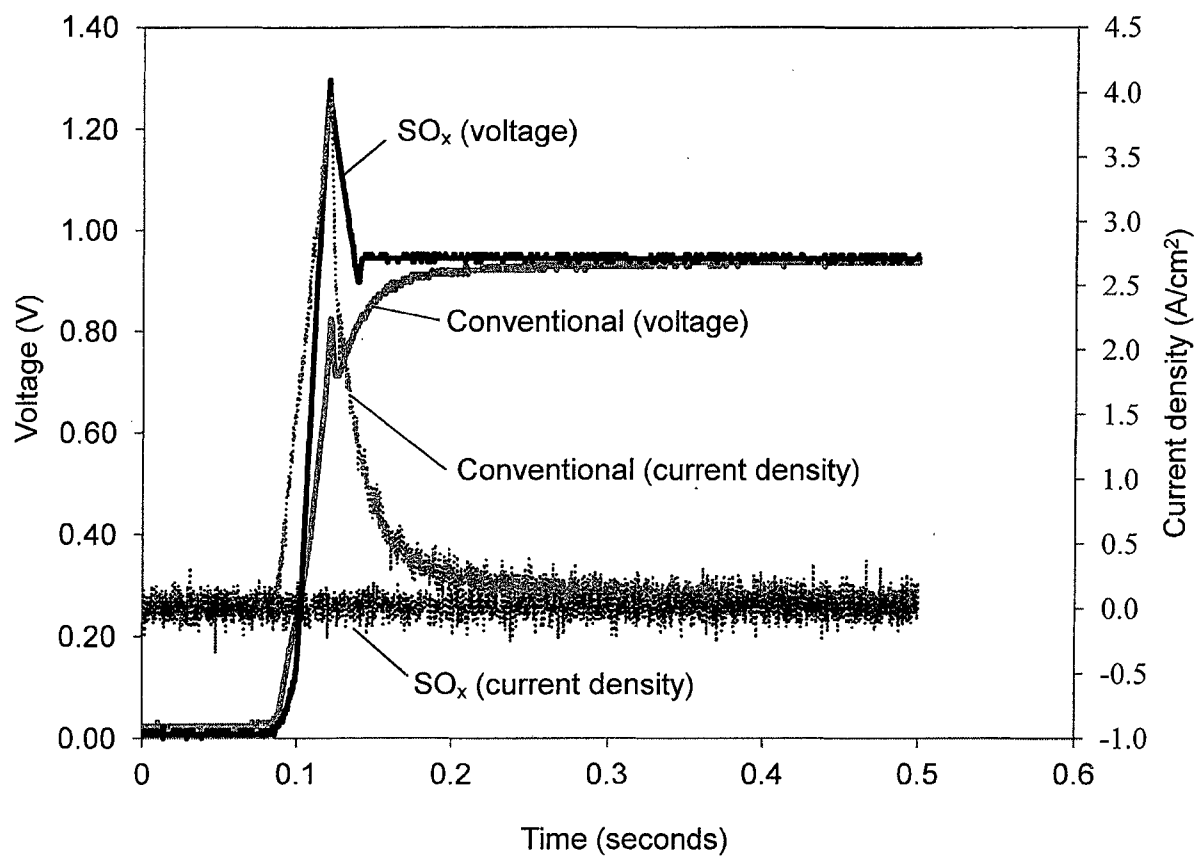


FIG. 1
Prior art

**FIG. 2**

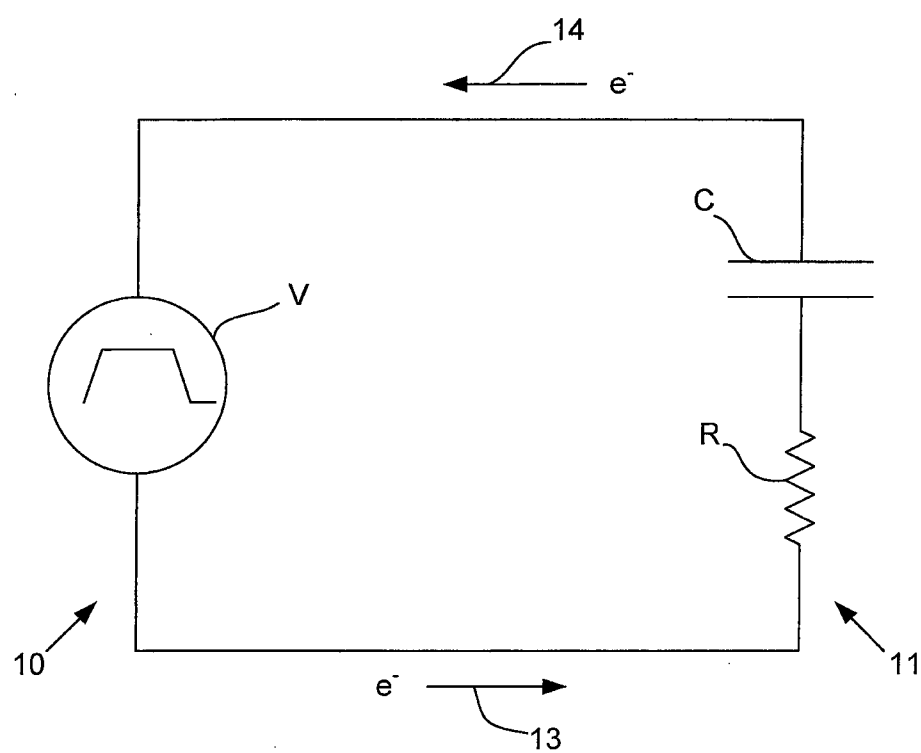


FIG. 3

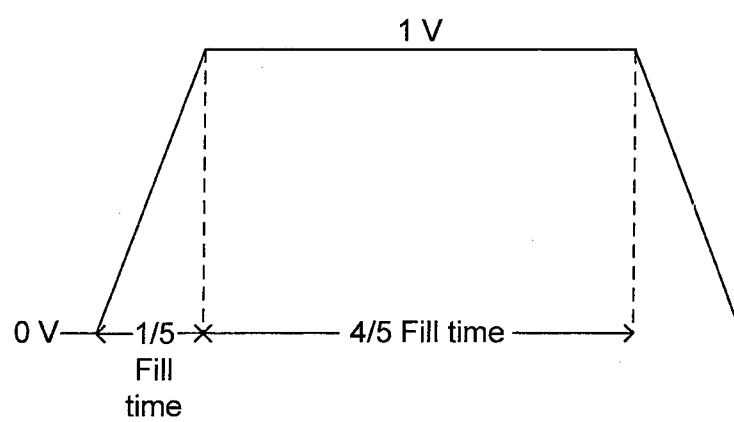
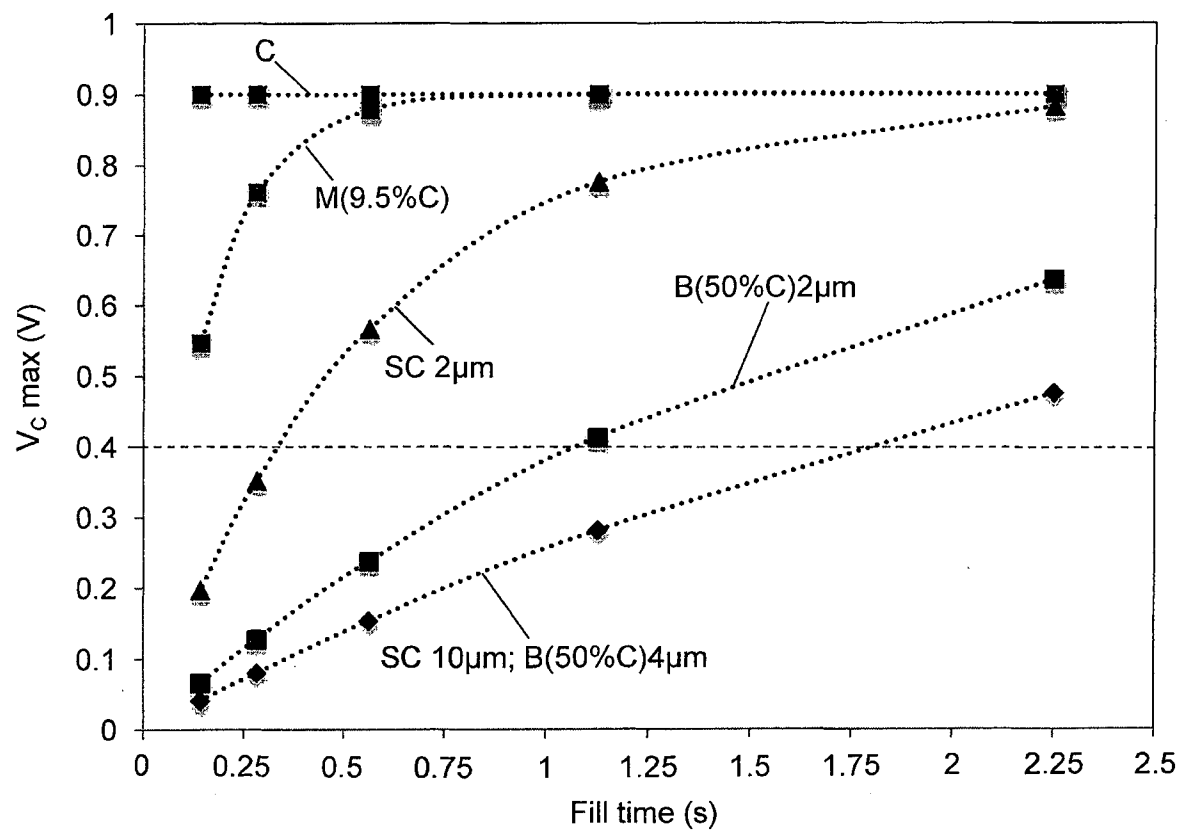


FIG. 3a

**FIG. 4**

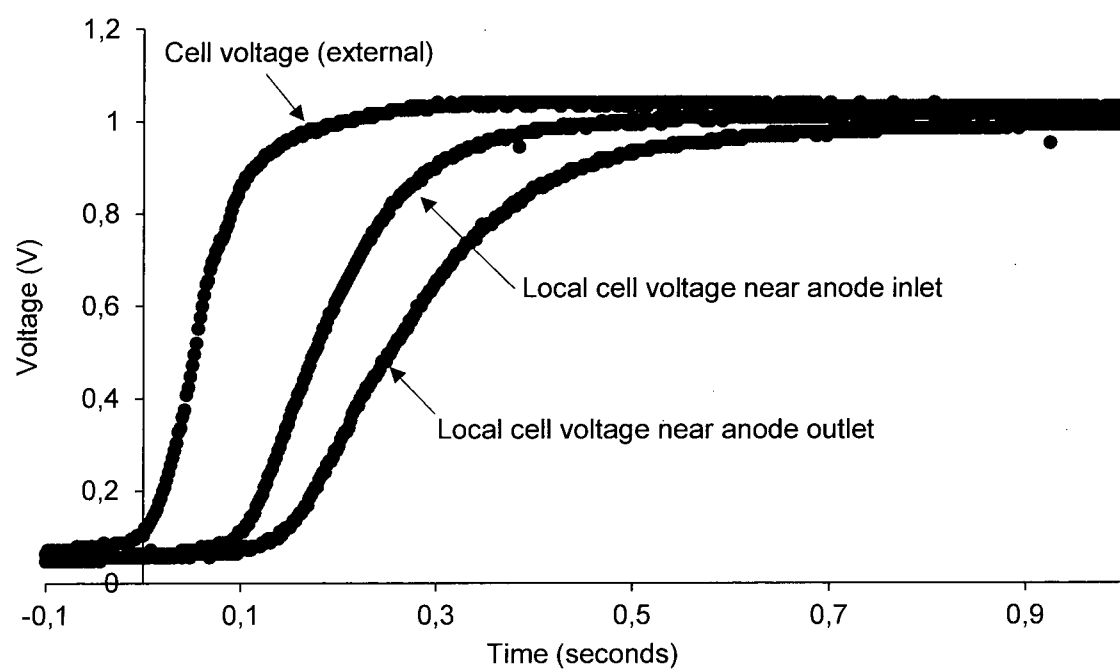


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/001646

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M8/0234 H01M8/0245 H01M8/04746 H01M8/04225
ADD. H01M8/1018

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 practicable, search terms used)

EP0-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.
Y	US 2015/325859 A1 (BERRETTA FRANCINE [CA] ET AL) 12 November 2015 (2015-11-12) cited in the application abstract paragraphs [0028] - [0040] claims 1-17	1,3-9
Y	US 2014/030625 A1 (HAAS HERWIG [CA] ET AL) 30 January 2014 (2014-01-30) cited in the application abstract paragraphs [0020] - [0029] claims 1-15	1,2,4-9
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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)

"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

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search

8 February 2017

Date of mailing of the international search report

15/02/2017

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/001646

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2003/134165 A1 (REISER CARL A [US] ET AL) 17 July 2003 (2003-07-17) cited in the application abstract paragraphs [0007] - [0015] claims 1-15 -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2016/001646

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015325859 A1	12-11-2015	DE 102015005350 A1	12-11-2015
		US 2015325859 A1	12-11-2015

US 2014030625 A1	30-01-2014	DE 102013012267 A1	06-03-2014
		US 2014030625 A1	30-01-2014

US 2003134165 A1	17-07-2003	AU 2002245084 A1	30-07-2002
		DE 10197086 B3	05-01-2017
		DE 10197086 T1	11-12-2003
		JP 4357836 B2	04-11-2009
		JP 2004523064 A	29-07-2004
		US 2002076582 A1	20-06-2002
		US 2003134165 A1	17-07-2003
		US 2005147855 A1	07-07-2005
		WO 02058168 A2	25-07-2002
