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- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
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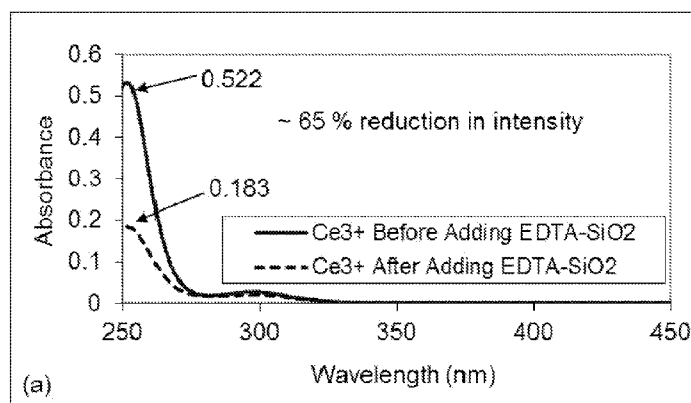
(54) **Title:** METHOD OF MAKING A MEMBRANE ELECTRODE ASSEMBLY

Figure 1.

(57) **Abstract:** A method of making a membrane electrode assembly for a fuel cell comprising: providing an anode, a cathode, and an ion-exchange membrane interposed therebetween; providing an electrically insulating oxide which is functionalized with an antioxidant or with a chelating agent which is complexed with an antioxidant to form an antioxidant additive; and applying the antioxidant additive to at least one of the anode, the cathode, and the ion-exchange membrane. The antioxidant is at least one of a radical scavenger, a hydrogen peroxide decomposition catalyst or a hydrogen peroxide stabilizer.



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METHOD OF MAKING A MEMBRANE ELECTRODE ASSEMBLY

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a method of making an antioxidant
5 additive for use in fuel cells, and more specifically to a method of making membrane
electrode assemblies having improved stability with an antioxidant additive.

Description of the Related Art

Fuel cell systems are currently being developed for use as power
supplies in numerous applications, such as automobiles and stationary power plants.
10 Such systems offer promise of delivering power economically and with environmental
and other benefits. To be commercially viable, however, fuel cell systems should
exhibit adequate reliability in operation, even when the fuel cells are subjected to
conditions outside their preferred operating ranges.

Fuel cells convert reactants, namely, fuel and oxidant, to generate
15 electric power and reaction products. Polymer electrolyte membrane fuel cells ("PEM
fuel cell") employ a membrane electrode assembly ("MEA"), which comprises a solid
polymer electrolyte or ion-exchange membrane disposed between the two electrodes,
namely a cathode and an anode. A catalyst typically induces the desired
electrochemical reactions at the electrodes. Separator plates, or flow field plates for
20 directing the reactants across one surface of each electrode substrate, are disposed on
each side of the MEA.

In operation, the output voltage of an individual fuel cell under load is
generally below one volt. Therefore, in order to provide greater output voltage,
multiple cells are usually stacked together and are connected in series to create a higher
25 voltage fuel cell stack. (End plate assemblies are placed at each end of the stack to hold
the stack together and to compress the stack components together. Compressive force
effects sealing and provides adequate electrical contact between various stack

components.) Fuel cell stacks can then be further connected in series and/or parallel combinations to form larger arrays for delivering higher voltages and/or currents.

In practice, fuel cells need to be robust to varying operating conditions, especially in applications that impose numerous on-off cycles and/or require dynamic, load-following power output, such as automotive applications. For example, one known failure mode that decreases lifetime relates to degradation of the ion-exchange membrane by, for example, reaction with reactive species such as hydrogen peroxide formed within the fuel cell environment. U.S. Pat. No. 6,335,112, U.S. Pat. No. 7,537,857, U.S. Pat. No. 8,367,267, U.S. Pat. No. 8,137,828, U.S. patent application No. 2003/0008196, U.S. patent application No. 2012/0225367, and Japanese Patent Application No. 2003-123777, all disclose the use of various catalysts for the decomposition of hydrogen peroxide species. These catalysts are dispersed in the ion-exchange membrane and/or in the cathode catalyst layer to improve lifetimes of hydrocarbon and fluorocarbon based ion-exchange membranes. However, such additives are prone to dissolution. For example, Coms et al. (*ECS Transactions*, 16 (2) 1735-1747 (2008)) found that after 200 hours of open circuit voltage testing, significant changes in the cerium concentration were observed. Most notably, the cerium concentration under the electrode area was reduced by about half as the cerium ion migrated beyond the active area to inactive areas of the membrane outside the electrode area. However, Coms et al. found no evidence indicating migration of Ce^{3+} out of the MEA during operation. More recently, Banham et al. (*ECS Transactions*, 58 (1) 369-380 (2013)) found that increasing the anode relative humidity during accelerated stress test cycling led to significantly higher end of life performance losses which was attributed to increased cerium oxide dissolution.

It is desirable to incorporate an additive to the fuel cell that mitigates the membrane degradation caused by the hydrogen peroxide formation and is stable over a range of operating conditions. The present description addresses this need and provides associated benefits.

BRIEF SUMMARY OF THE INVENTION

In brief, a method of making a membrane electrode assembly comprises providing an anode, a cathode, and an ion-exchange membrane interposed therebetween; providing an electrically insulating oxide and immobilizing an antioxidant to the surface of the electrically insulating oxide to form an antioxidant additive; and applying the antioxidant additive to at least one of the anode, the cathode, or the ion-exchange membrane.

In one embodiment, the step of immobilizing the antioxidant to the surface of the electrically insulating oxide comprises functionalizing the electrically insulating oxide with the antioxidant to form the antioxidant additive, wherein the antioxidant is at least one of a radical scavenger, a hydrogen peroxide decomposition catalyst or a hydrogen peroxide stabilizer.

In another embodiment, the step of immobilizing the antioxidant to the surface of the electrically insulating oxide comprises functionalizing the electrically insulating oxide with a chelating agent, which is then complexed with the antioxidant to form the antioxidant additive, wherein the antioxidant is at least one of the radical scavenger or the hydrogen peroxide decomposition catalyst.

In some embodiments the chelating agent is ethylenediaminetetraacetic acid (EDTA). In other embodiments, other chelating agents may be used in place of EDTA, such as thiols, thiourea, and sulfonates. In some embodiments the electrically insulating oxide is silica. Alternatively, other electrically insulating oxides may be used in place of silica, such as titanium dioxide, yttrium oxide, zirconium dioxide, and niobium pentoxide.

In some embodiments, the anode comprises an anode gas diffusion layer and an anode catalyst layer, and the cathode comprises a cathode gas diffusion layer and a cathode catalyst layer.

In some embodiments, applying the antioxidant additive comprises dispersing the antioxidant additive within the at least one of the anode gas diffusion layer, the anode catalyst layer, the cathode gas diffusion layer, the cathode catalyst layer, or within an ionomer of the ion-exchange membrane and, in other embodiments,

applying the antioxidant additive comprises applying a layer of antioxidant additive on a surface of the at least one of the anode gas diffusion layer, the anode catalyst layer, the cathode gas diffusion layer, the cathode catalyst layer, or the ion-exchange membrane.

5 The antioxidant additive may be either uniformly or non-uniformly dispersed within the anode gas diffusion layer, the anode catalyst, the cathode gas diffusion layer and/or the cathode catalyst layer, or within the ion-exchange membrane.

 For example, the concentration of the antioxidant additive may vary through the thickness of the anode gas diffusion layer, the anode catalyst layer, the
10 cathode gas diffusion layer, the cathode catalyst layer and/or the ion-exchange membrane.

 In some embodiments, the antioxidant additive may be applied to the ion-exchange membrane by mixing the antioxidant additive with the ionomer of the ion-exchange membrane prior to casting during the manufacturing process of the ion-
15 exchange membrane.

 In some embodiments, more than one type of antioxidant additive or mixtures thereof may be applied to any of the anode, the cathode and/or the ion-exchange membrane.

 In some embodiments, the radical scavenger is selected from the group
20 consisting of hindered amines, hydroxylamines, arylamines, phenols, butylated hydroxytoluene, phosphites, benzofuranones, salicylic acid, azulenyl nitrones and derivatives thereof, tocopherols, 5,5-dimethyl-1-pyrroline-N-oxide, cyclic and acyclic nitrones, gold-chitosan nanocomposites, ascorbic acid and Mn^{2+} .

 In some embodiments, the hydrogen peroxide decomposition catalyst is
25 a lanthanide series metal cation and, in a more specific embodiment, the lanthanide series metal cation is at least one of cerium and lanthanum, and mixtures thereof.

 In one embodiment, the antioxidant additive is Ce/EDTA-SiO_2 .

 These and other aspects of the invention are evident upon reference in the attached drawings and following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the results from UV-visible spectroscopy of Ce/EDTA-SiO₂.

Figure 2 shows the results from UV-visible spectroscopy of Ce/HSO₃-
5 SiO₂.

Figure 3 shows the fluoride release rate as a function of AST operation time of baseline MEAs as compared to MEAs with Ce/EDTA-SiO₂.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In the following description, certain specific details are set forth in order
10 to provide a thorough understanding of the various embodiments of the invention. However, one skilled in the art will understand that the invention may be practiced without these details. In other instances, well-known structures associated with fuel cells, fuel cell stacks, batteries and fuel cell systems have not been shown or described in detail to avoid unnecessarily obscuring descriptions of the embodiments of the
15 invention.

Unless the context requires otherwise, throughout the specification and claims which follow, the word “comprise” and variations thereof, such as, “comprises” and “comprising” are to be construed in an open, inclusive sense, that is, as “including, but not limited to.”

20 In this application, the term "polymer" is also meant to include copolymer and oligomer.

Furthermore, the term "acid" is meant to include substances that donate a proton in a chemical reaction to a base. The term "acid derivative" is meant to include materials that behave similarly to acids such as acid salts, and acid esters, particularly
25 lower alkyl esters containing from 1 to 4 carbon atoms.

A “corrosion resistant support material” is at least as resistant to oxidative corrosion as Shawinigan acetylene black (Chevron Chemical Company, TX, USA).

As discussed, additives for mitigating the effects of the hydrogen peroxide formation typically experience dissolution during fuel cell operation due to high relative humidity, as well as their high solubility at low or high potential, and/or low pH. The present description relates to a method of making a membrane electrode assembly (MEA) having an anode, a cathode, and an ion-exchange membrane interposed therebetween by applying to the anode, the cathode and/or the ion-exchange membrane at least one antioxidant additive which mitigates the membrane degradation caused by the hydrogen peroxide formation, more specifically an antioxidant additive which mitigates the membrane degradation caused by the hydroxyl and/or hydroperoxyl radicals formed during the fuel cell operation either directly or through the decomposition of hydrogen peroxide.

The present method of making an MEA comprises providing an electrically insulating oxide, immobilizing an antioxidant to the surface of the electrically insulating oxide to form an antioxidant additive and applying the antioxidant additive to at least one of the anode, the cathode and the ion-exchange membrane. In this application the term “immobilizing” is meant to include either functionalizing the electrically insulating oxide with the antioxidant by chemical bonding or functionalizing the electrically insulating oxide with a chelating agent which is then complexed with an antioxidant to form the antioxidant additive.

In one embodiment, the electrically insulating oxide is silica and the method of making an MEA comprises functionalizing the silica with a chelating agent such as the ethylenediaminetetraacetic acid (EDTA), complexing the EDTA with an antioxidant which can be at least one of a radical scavenger or a hydrogen peroxide decomposition to form an antioxidant additive, and applying the antioxidant additive to at least one of the anode, the cathode or the ion-exchange membrane. The inventors have discovered that by binding at least one of a radical scavenger or a hydrogen peroxide decomposition catalyst to EDTA-functionalized silica to form an antioxidant additive, and then applying the antioxidant additive to the MEA, membrane degradation caused by the hydroxyl and/or hydroperoxyl radicals which can form either directly or through the decomposition of the hydrogen peroxide formed during the fuel cell

operation was greatly reduced while fuel cell performance was unaffected. One advantage of forming the antioxidant additive prior to incorporating it into the anode, cathode, and/or ion-exchange membrane is that the loading and composition of the antioxidant additive can be verified and controlled.

5 In another embodiment, the method of making an MEA comprises functionalizing an electrically insulating oxide, for example silica, with an antioxidant which is at least one of a radical scavenger, a hydrogen peroxide decomposition catalyst or a hydrogen peroxide stabilizer to thereby form the antioxidant additive and applying the antioxidant additive to at least one of the anode, the cathode or the ion exchange
10 membrane.

 One skilled in the art will appreciate that the loading of the radical scavenger, the hydrogen peroxide decomposition catalyst and/or the hydrogen peroxide stabilizer on the electrically insulating oxide will vary depending on the composition of the radical scavenger, the hydrogen peroxide decomposition catalyst and/or the
15 hydrogen peroxide stabilizer, as well as the expected fuel cell conditions to which the MEA will be subjected. For example, the loading of the radical scavenger, the hydrogen peroxide decomposition catalyst and/or the hydrogen peroxide stabilizer may range from about 0.05 g/m² to about 1 g/m², and preferably from about 0.05 g/m² to about 0.5 g/m².

20 In some embodiments, other electrically insulating oxides may be used in place of silica, such as titanium dioxide, yttrium oxide, zirconium dioxide, and niobium pentoxide. Without being bound by theory, insulating oxides are preferred as they protect the chelating agent from oxidative degradation.

 In some embodiments, other chelating agents may be used in place of
25 EDTA, such as thiols, thiourea, and sulfonates, as well as those described in U.S. Patent Publication No. 2011/0111321, PCT Publication No. 2012/136348 and Canadian Patent Publication No. 2835783.

 In some embodiments, the radical scavenger may be selected from hindered amines, hydroxylamines, arylamines, phenols, butylated hydroxytoluene,
30 phosphites, benzofuranones, salicylic acid, azulenyl nitrones and derivatives thereof,

tocopherols, 5,5-dimethyl-1-pyrroline-N-oxide, cyclic and acyclic nitrones, gold-chitosan nanocomposites, ascorbic acid and Mn^{2+} .

In some embodiments, the hydrogen peroxide decomposition catalyst is a lanthanide series metal cation, such as cerium, lanthanum, or mixtures thereof.

5 In some embodiments, more than one type of antioxidant additive may be used in any of the anode, the cathode, and the membrane. In one example, mixtures of different antioxidant additives may be used. In another example, different antioxidant additives may be used for each of the anode, the cathode, and the ion-exchange membrane.

10 The anode and cathode catalyst may be any suitable fuel cell catalyst, such as platinum, gold, ruthenium, silver, cobalt, molybdenum, iridium, tantalum, iron, palladium, osmium, tin, tungsten, nickel, and compounds, alloys, solid solutions, and mixtures thereof. In embodiments where a Pt alloy catalyst is employed, the alloy may include another noble metal (*e.g.*, Pt-Au) or a non-noble metal (*e.g.*, Pt-Mo, Pt-Co-Ir,
15 Pt-Ni, and Pt-Pd).

The anode and cathode catalyst may either be unsupported or supported in dispersed form on a suitable electrically conducting particulate support. Preferably, the support used is itself tolerant to degradation from voltage reversal and carbon corrosion. Thus, it is desirable to consider using carbon supports that are more
20 corrosion resistant.

The corrosion resistant support material may comprise carbon, if desired. High surface area carbons such as acetylene or furnace blacks are commonly used as supports for such catalysts. Generally, the corrosion resistance of a carbon support material is related to its graphitic nature: the more graphitic the carbon support, the
25 more corrosion resistant it is. Graphitized carbon BA (TKK, Tokyo, JP) has a similar BET surface area to Shawinigan acetylene carbon and is a suitable carbon support material in some embodiments. In other embodiments, suitable carbon support materials may include boron and/or phosphorous-doped carbons, carbon nanofibres, carbon nanotubes, and aerogels.

Instead of carbon, carbides or electrically conductive metal oxides may be considered as a suitable high surface area support for the corrosion resistant support material. For instance, titanium and niobium oxides may serve as a corrosion resistant support material in some embodiments. In this regard, other valve metal oxides might
5 be considered as well if they have acceptable electronic conductivity when acting as catalyst supports.

In embodiments where the anode and/or cathode catalyst is supported, the loading of the catalyst on the support material is from 20 – 80% by weight, typically 20 – 50% by weight. Though a lower catalyst loading on the support is typically
10 preferred in terms of electrochemical surface area per gram of platinum (ECA), a higher catalyst loading and coverage of the support appears preferable in terms of reducing corrosion of the support and in reducing catalyst loss during fuel cell operation.

In some embodiments, the amount of anode and/or cathode catalyst that is desirably incorporated will depend on such factors as the fuel cell stack construction and operating conditions, cost, desired lifetime, and so on. For example, the loading of
15 the catalyst may range from about 0.01 mg Pt/cm² on the low end for the anode electrode to about 0.8 mg Pt/cm² on the high end for the cathode electrode. It is expected that some empirical trials will determine an optimum amount for a given application.

20 The antioxidant additive may be incorporated into the electrode in various ways. In some embodiments, the anode and/or cathode catalyst may be mixed with the antioxidant additive and formed into an ink, which is then applied in a uniformly distributed common layer or layers on a suitable gas diffusion layer (GDL), ion-exchange membrane, or decal transfer sheet. With decal transfer, the layer is decal
25 transferred from the decal transfer sheet to a GDL to form a gas diffusion electrode, or decal transferred to a solid electrolyte membrane to form a catalyst-coated membrane (CCM). In further embodiments, the anode and/or cathode catalyst and the antioxidant additive may instead be applied in separate layers on a GDL, ion-exchange membrane, or decal transfer sheet, thereby making a bilayer or multilayer structure where the anode
30 and/or cathode catalyst and the antioxidant additive are in discrete layers. In some

embodiments, the antioxidant additive may be incorporated as a layer between the gas diffusion layer and the catalyst layer. In other embodiments, the antioxidant additive may be incorporated as a layer between the catalyst layer and the solid electrolyte membrane.

5 In some embodiments, the antioxidant additive may be uniformly or non-uniformly distributed in the GDL and/or catalyst layer. For example, the concentration of the antioxidant additive may vary through the thickness of the GDL and/or catalyst layer. Additionally, or alternatively, the concentration of the antioxidant additive may vary along the x-y plane of the GDL and/or catalyst layer. The manner of
10 incorporating the antioxidant additive is not essential, and persons of ordinary skill in the art can readily select an appropriate manner of incorporation for a given application.

The anode and cathode catalyst layers typically further comprise a binder, such as an ionomer and/or hydrophobic agent.

In some embodiments, the through-plane concentration of ionomer in the
15 anode and/or cathode catalyst layers decrease as a function of distance from the membrane interface. The presence of ionomer in the anode and/or cathode catalyst layers effectively increases the electrochemically active surface area of the catalyst, which requires an ionically conductive pathway to the cathode catalyst to generate electric current. In the case of a hydrophobic agent, the hydrophobic agent may
20 comprise a fluororesin or other suitable polymer, as desired. Examples of suitable fluororesins include terpolymers of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene, copolymers of ethylene and tetrafluoroethylene, copolymers of hexafluoropropylene and tetrafluoroethylene, polyvinylidene fluorides, and polytetrafluoroethylenes. For example, the anode binder often contains a dispersion of
25 polytetrafluoroethylene (PTFE) or other hydrophobic polymer, such as described in U.S. 5,395,705, and may also include a filler (*e.g.*, carbon).

As previously mentioned, the layers of catalyst mixed with the antioxidant additive or the separate layers of catalyst and antioxidant additive may be applied to a GDL to form anode and cathode electrodes, or to a decal transfer sheet,
30 with or without catalyst, which is then decal transferred to a surface of the GDL or ion-

exchange membrane, or applied directly to the surface of the ion-exchange membrane to form a CCM. The electrodes or CCM can then be bonded with other components to form an MEA. Alternatively, the application of the layer on the desired substrate may occur at the same time the remaining MEA components are bonded together.

5 The present layers may be applied according to known methods. For example, the compositions may be applied as an ink or slurry, or as a dry mixture. Such inks may be applied using a variety of suitable techniques (*e.g.*, hand and machine methods, including spraying, hand brushing, notch bar coating, fluid bearing die coating, wire-wound rod coating, fluid bearing coating, slot-fed knife coating, three-roll
10 coating, screen-printing and decal transfer) to the surface of the ion-exchange membrane or GDL. Examples of dry deposition methods include electrostatic powder deposition techniques and decal transfer.

Inks typically incorporate the compositions and binder in a solvent/dispersant to form a solution, dispersion or colloidal mixture. Suitable
15 solvents/dispersants include water, organic solvents such as alcohols and polar aprotic solvents (*e.g.*, N-methylpyrrolidinone, dimethylsulfoxide, and N,N-dimethylacetamide), and mixtures thereof. Depending on the amount of water, one can distinguish water-based inks, wherein water forms the major part of the solvents used, from inks wherein organic solvents form the major part. The inks may further include surfactants and/or
20 pore forming agents, if desired. Suitable pore formers include methyl cellulose; sublimating pore-forming agents such as durene, camphene, camphor and naphthalene; and pore-forming solvents that are immiscible with the catalyst ink solvent/dispersant, such as n-butyl acetate in polar aprotic solvent/dispersant systems.

Additionally, or alternatively, the antioxidant additive may be
25 incorporated into the membrane by mixing the antioxidant additive with the ionomer prior to casting into membrane form. The antioxidant additive can be uniformly or non-uniformly distributed within the membrane. In some embodiments, the concentration of the antioxidant additive within the membrane can vary across the membrane thickness or along the x-y plane of the membrane.

The selection of additional components for the mixture and the choice of application method and GDL to which it is applied are not essential to the present invention, and will depend on the physical characteristics of the mixture and the substrate to which it will be applied, the application method and desired structure of the catalyst layer. Persons of ordinary skill in the art can readily select suitable catalyst mixtures and application methods for a given application.

EXAMPLES

Preparation of the Ce/EDTA-SiO₂ Antioxidant Additive

When preparing the Ce/EDTA-SiO₂ antioxidant additive, it was assumed that the cerium cations would bind with the EDTA in a 1:1 molar ratio. Thus, for 2 g of EDTA-SiO₂ having a molar loading of 0.48 mmol/g (mmol EDTA/g SiO₂), 0.417 g of Ce(NO₃)₃·6H₂O would be required to fully load the EDTA-SiO₂. To ensure that the loading was complete, 0.625 g of Ce(NO₃)₃·6H₂O was used (1.5 x more than required for a complete loading) with 2 g of EDTA-SiO₂.

The cerium cation solution was prepared by dissolving the Ce(NO₃)₃·6H₂O in 20 mL of H₂O. The EDTA-SiO₂ was then added to this solution, followed by 2 h of stirring. After stirring, the suspension was centrifuged, and the Ce/EDTA-SiO₂ material was collected.

UV-Visible Spectroscopy

In order to verify that the cerium cations had been captured in the assumed 1:1 molar ratio by the EDTA-SiO₂, UV-visible spectroscopy was used to measure the cerium cation concentration before and after adding the EDTA-SiO₂ (see Figure 1). Since the cerium cation concentration was intentionally made 1.5x higher than required to fully load the EDTA-SiO₂, it was expected that the solution remaining after centrifuging and collecting the Ce/EDTA-SiO₂ should still contain some cerium cations. Specifically, if a 1:1 loading was actually achieved, 33.3 % of the cerium cations should still be present in the solution that was collected after centrifuging. As

shown in Figure 1, this was observed, with the UV-visible spectroscopy signal showing a decrease of $\sim 65\%$ following the addition of EDTA-SiO₂. Importantly, this confirms that the EDTA-SiO₂ strongly bound to the cerium cations, and that the assumed 1:1 molar ratio between cerium cations and EDTA was correct.

5 For comparison, the same experiment was performed with a weakly binding functional group (HSO₃-SiO₂). As clearly shown in Figure 2, the HSO₃ was unable to bind with the cerium cations (no change in the UV-visible spectroscopy signal was observed after adding the HSO₃-SiO₂).

Fuel Cell Testing

10 In order to evaluate the impact of the Ce/EDTA-SiO₂ on membrane lifetime, the Ce/EDTA-SiO₂ was dispersed in a Nafion solution and sprayed onto a Pt-based anode and cathode catalyst film. For both the anode and cathode, a Ce/EDTA-SiO₂ loading of 2 g/m² was used with a Nafion loading of 1 g/m². Due to the relatively low molar loading of EDTA on the SiO₂, this translates to a cerium loading of 0.13
15 g/m². A catalyst-coated membrane was then prepared by decaling the anode and cathode catalyst layer to a Nafion (NR211) membrane so that the Ce/EDTA-SiO₂ is a thin layer between the membrane and the adjacent catalyst layers.

To evaluate the membrane durability, a 5 cell stack was first subjected to a beginning of life conditioning procedure for initial electrochemical activation of the
20 MEAs by applying a medium current density (0.5 A/cm²) in pure hydrogen at the anode and air at the cathode. The durability test included a cyclic open circuit voltage accelerated stress test (AST) which involves an open circuit voltage (OCV) phase under high temperature/low RH conditions, followed by a series of wet/dry cycling. The test was performed until at least 3 out of 5 MEAs have failed.

25 Accumulated fluoride release as a function of AST operation time as well as the number of AST cycles were compared for the MEAs with and without Ce/EDTA-SiO₂ (see Figure 3). MEA samples with Ce/EDTA-SiO₂ showed an improvement in chemical stability by having 13 times lower fluoride releases compare to baseline MEAs (*i.e.*, without the Ce/EDTA-SiO₂ antioxidant additive). The rest of

MEAs with Ce/EDTA-SiO₂ is still in progress and to date these MEAs show 5 times longer lifetime compared to baseline MEAs.

While the present membrane electrode assemblies have been described for use in PEM fuel cells, it is anticipated that they would be useful in other fuel cells
5 having an operating temperature below about 250 °C. They are particularly suited for acid electrolyte fuel cells, including phosphoric acid, PEM and liquid feed fuel cells.

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 and/or listed in the Application Data Sheet,
10 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, particularly in light of the foregoing teachings. It is therefore contemplated by the
15 appended claims to cover such modifications that incorporate those features coming within the scope of the invention.

This application also claims the benefit of U.S. Provisional Patent Application No. 62/155,658, filed May 1, 2015, and is incorporated herein by reference in its entirety.

CLAIMS

What is claimed is:

1. A method of making a membrane electrode assembly for a fuel cell comprising:
 - providing an anode, a cathode, and an ion-exchange membrane interposed therebetween;
 - providing an electrically insulating oxide and immobilizing an antioxidant to the surface of the electrically insulating oxide to form an antioxidant additive; and
 - applying the antioxidant additive to at least one of the anode, the cathode, or the ion-exchange membrane.
2. The method of claim 1 wherein immobilizing the antioxidant to the surface of the electrically insulating oxide comprises functionalizing the electrically insulating oxide with the antioxidant to form the antioxidant additive, and wherein the antioxidant is at least one of a radical scavenger, a hydrogen peroxide decomposition catalyst or a hydrogen peroxide stabilizer.
3. The method of claim 1 wherein immobilizing the antioxidant to the surface of the electrically insulating oxide comprises functionalizing the electrically insulating oxide with a chelating agent, which is then complexed with the antioxidant to form the antioxidant additive, and wherein the antioxidant is at least one of the radical scavenger or the hydrogen peroxide decomposition catalyst.
4. The method of claim 3 wherein the chelating agent is selected from ethylenediaminetetraacetic acid, thiols or thiourea.

5. The method of claim 1 wherein the electrically insulating oxide is selected from silica, titanium dioxide, yttrium oxide, zirconium dioxide and niobium pentoxide.

6. The method of claim 2, wherein the radical scavenger is selected from hindered amines, hydroxylamines, arylamines, phenols, butylated hydroxytoluene, phosphites, benzofuranones, salicylic acid, azulenyl nitrones and derivatives thereof, tocopherols, 5,5-dimethyl-1-pyrroline-N-oxide, cyclic and acyclic nitrones, gold-chitosan nanocomposites, ascorbic acid and Mn^{2+} .

7. The method of claim 3, wherein the radical scavenger is selected from hindered amines, hydroxylamines, arylamines, phenols, butylated hydroxytoluene, phosphites, benzofuranones, salicylic acid, azulenyl nitrones and derivatives thereof, tocopherols, 5,5-dimethyl-1-pyrroline-N-oxide, cyclic and acyclic nitrones, gold-chitosan nanocomposites, ascorbic acid and Mn^{2+} .

8. The method of claim 2, wherein the hydrogen peroxide decomposition catalyst is a lanthanide series metal cation.

9. The method of claim 8 wherein the lanthanide series metal cation is at least one of cerium and lanthanum, and mixtures thereof.

10. The method of claim 3, wherein the hydrogen peroxide decomposition catalyst is a lanthanide series metal cation, which is at least one of cerium and lanthanum, and mixtures thereof.

11. The method of claim 10 wherein the lanthanide series metal cation is at least one of cerium and lanthanum, and mixtures thereof.

12. The method of claim 1, wherein the anode comprises an anode gas diffusion layer and an anode catalyst layer, and the cathode comprises a cathode gas diffusion layer and a cathode catalyst layer.

13. The method of claim 12, wherein applying the antioxidant additive comprises dispersing the antioxidant additive within at least one of the anode gas diffusion layer, the anode catalyst layer, the cathode diffusion layer, the cathode catalyst layer, or within an ionomer of the ion-exchange membrane.

14. The method of claim 13 wherein the antioxidant additive may be non-uniformly dispersed within at least one of the anode gas diffusion layer, the anode catalyst layer, the cathode gas diffusion layer, the cathode catalyst layer or the ion-exchange membrane.

15. The method of claim 14 wherein the concentration of the antioxidant additive may vary through the thickness of at least one of the anode gas diffusion layer, the anode catalyst layer, the cathode gas diffusion layer, the cathode catalyst layer, or the ion-exchange membrane.

16. The method of claim 13 wherein applying the antioxidant additive comprises mixing the antioxidant additive with the ionomer prior to casting the ion-exchange membrane.

17. The method of claim 12, wherein applying the antioxidant additive comprises applying a layer of the antioxidant additive on a surface of at least one of the anode gas diffusion layer, the anode catalyst layer, the cathode diffusion layer, the cathode catalyst layer, or the ion-exchange membrane.

18. The method of claim 1, wherein more than one type of antioxidant additive or mixtures thereof may be applied to at least one of the anode, the cathode, or the ion-exchange membrane.

AMENDED CLAIMS
received by the International Bureau on 31 August 2016 (31.08.2016)

What is claimed is:

1. A method of making a membrane electrode assembly for a fuel cell comprising:

providing an anode, a cathode, and an ion-exchange membrane interposed therebetween;

providing an electrically insulating oxide and immobilizing an antioxidant to the surface of the electrically insulating oxide to form an antioxidant additive; and

applying the antioxidant additive to at least one of the anode, the cathode, or the ion-exchange membrane;

wherein immobilizing the antioxidant to the surface of the electrically insulating oxide comprises functionalizing the electrically insulating oxide with a chelating agent, which is then complexed with the antioxidant to form the antioxidant additive, and wherein the antioxidant is at least one of the radical scavenger or the hydrogen peroxide decomposition catalyst;

wherein the chelating agent is selected from ethylenediaminetetraacetic acid, thiols or thiourea.

2. The method of claim 1, wherein immobilizing the antioxidant to the surface of the electrically insulating oxide comprises functionalizing the electrically insulating oxide with the antioxidant to form the antioxidant additive, and wherein the antioxidant is at least one of a radical scavenger, a hydrogen peroxide decomposition catalyst or a hydrogen peroxide stabilizer.

3. The method of claim 1, wherein the electrically insulating oxide is selected from silica, titanium dioxide, yttrium oxide, zirconium dioxide and niobium pentoxide.

4. The method of claim 2, wherein the radical scavenger is selected from hindered amines, hydroxylamines, arylamines, phenols, butylated hydroxytoluene, phosphites, benzofuranones, salicylic acid, azulenyl nitrones and derivatives thereof, tocopherols, 5,5-dimethyl-1-pyrroline-N-oxide, cyclic and acyclic nitrones, gold-chitosan nanocomposites, ascorbic acid and Mn^{2+} .

5. The method of claim 1, wherein the radical scavenger is selected from hindered amines, hydroxylamines, arylamines, phenols, butylated hydroxytoluene, phosphites, benzofuranones, salicylic acid, azulenyl nitrones and derivatives thereof, tocopherols, 5,5-dimethyl-1-pyrroline-N-oxide, cyclic and acyclic nitrones, gold-chitosan nanocomposites, ascorbic acid and Mn^{2+} .

6. The method of claim 2, wherein the hydrogen peroxide decomposition catalyst is a lanthanide series metal cation.

7. The method of claim 6, wherein the lanthanide series metal cation is at least one of cerium and lanthanum, and mixtures thereof.

8. The method of claim 1, wherein the hydrogen peroxide decomposition catalyst is a lanthanide series metal cation, which is at least one of cerium and lanthanum, and mixtures thereof.

9. The method of claim 8, wherein the lanthanide series metal cation is at least one of cerium and lanthanum, and mixtures thereof.

10. The method of claim 1, wherein the anode comprises an anode gas diffusion layer and an anode catalyst layer, and the cathode comprises a cathode gas diffusion layer and a cathode catalyst layer.

11. The method of claim 10, wherein applying the antioxidant additive comprises dispersing the antioxidant additive within at least one of the anode gas diffusion layer, the anode catalyst layer, the cathode diffusion layer, the cathode catalyst layer, or within an ionomer of the ion-exchange membrane.

12. The method of claim 11, wherein the antioxidant additive may be non-uniformly dispersed within at least one of the anode gas diffusion layer, the anode catalyst layer, the cathode gas diffusion layer, the cathode catalyst layer or the ion-exchange membrane.

13. The method of claim 12, wherein the concentration of the antioxidant additive may vary through the thickness of at least one of the anode gas diffusion layer, the anode catalyst layer, the cathode gas diffusion layer, the cathode catalyst layer, or the ion-exchange membrane.

14. The method of claim 11, wherein applying the antioxidant additive comprises mixing the antioxidant additive with the ionomer prior to casting the ion-exchange membrane.

15. The method of claim 10, wherein applying the antioxidant additive comprises applying a layer of the antioxidant additive on a surface of at least one of the anode gas diffusion layer, the anode catalyst layer, the cathode diffusion layer, the cathode catalyst layer, or the ion-exchange membrane.

16. The method of claim 1, wherein more than one type of antioxidant additive or mixtures thereof may be applied to at least one of the anode, the cathode, or the ion-exchange membrane.

1 / 2

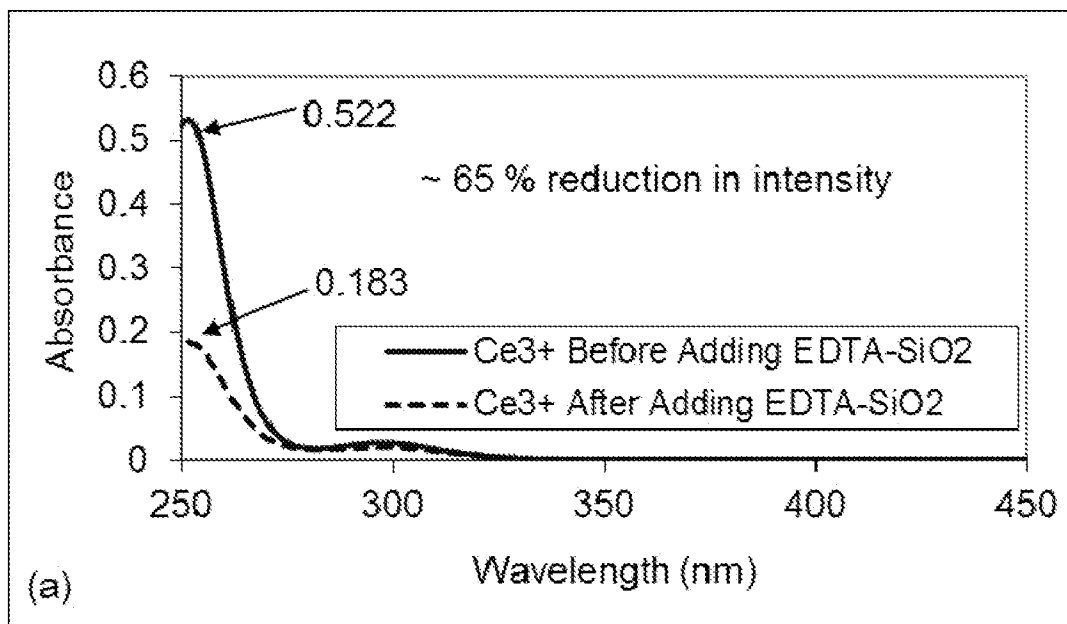


Figure 1.

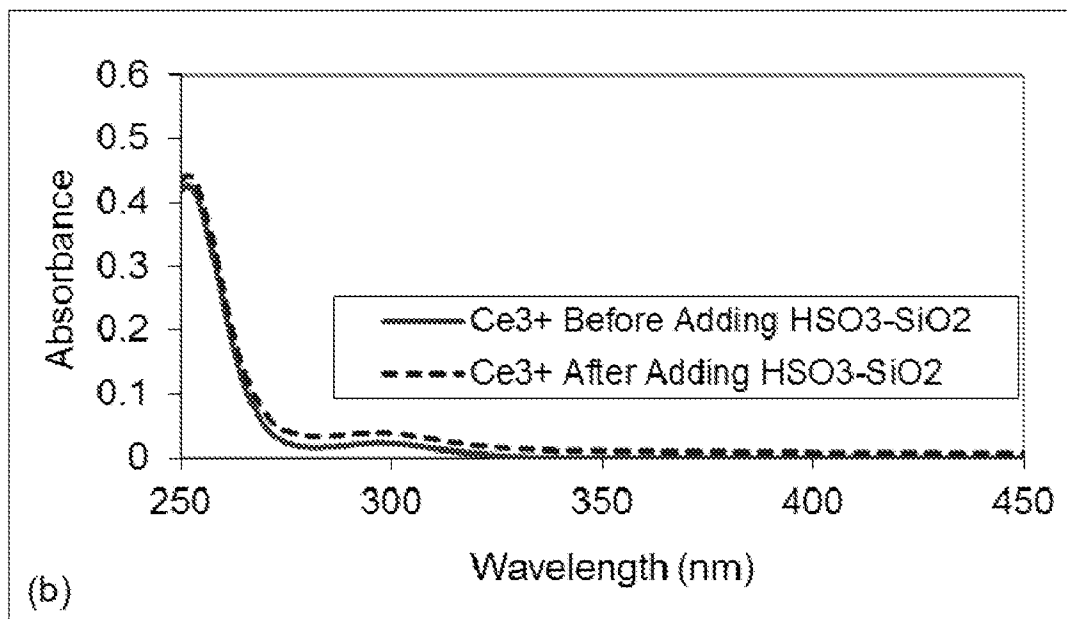


Figure 2.

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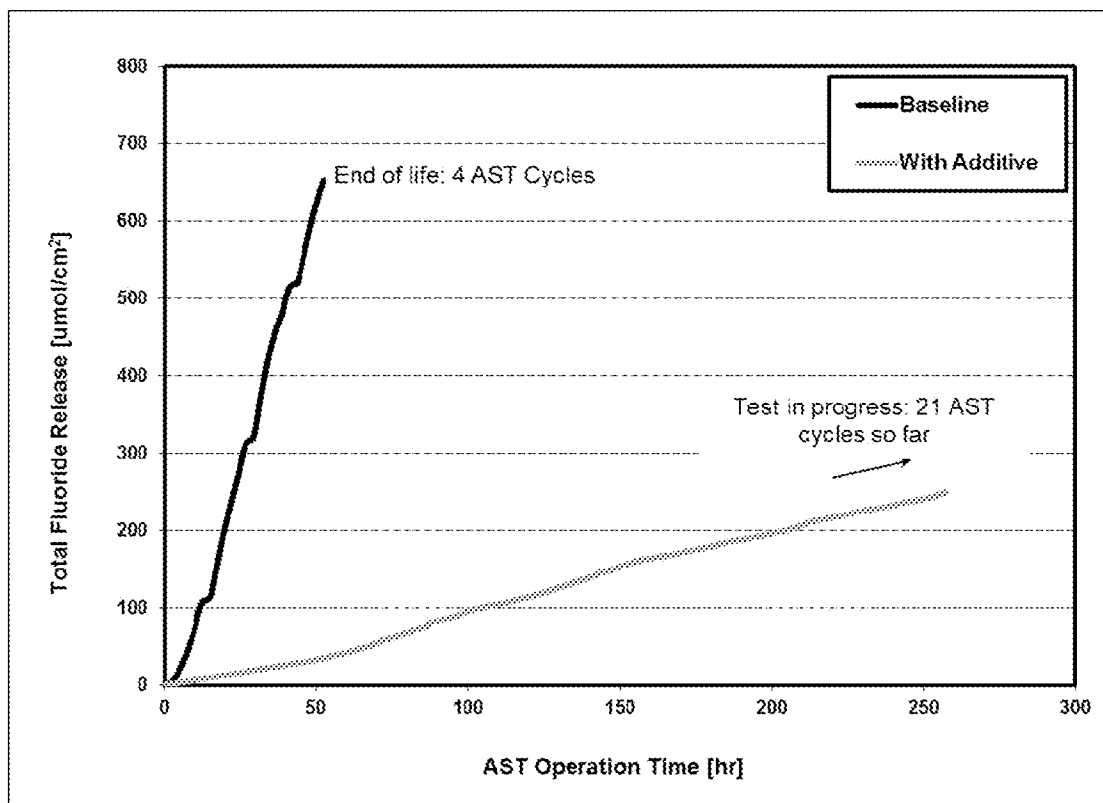


Figure 3.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/029230

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M8/1004 H01M4/90
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

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Y	claims 1-5,7,9-11,14 table 2 paragraphs [0001], [0007], [0008], [0012], [0014], [0015], [0019], [0027], [0028], [0031], [0048], [0051]	6,7
X	US 2009/155662 A1 (DELANEY W; DELANEY W E; DELRANI W I; DURANTE V; DURANTE V A; DYURANTE) 18 June 2009 (2009-06-18) claims 5,9,10,14,15,20,22,23,25,26,31,34,36,38,39 ,41,45 claims 47,49,50,51,52,56,57,60,61,63,64 figure 1 paragraphs [0011], [0035] - [0039], [0095]	1-18



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"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

22 June 2016

Date of mailing of the international search report

01/07/2016

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/029230

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	EP 1 702 378 A1 (BALLARD POWER SYSTEMS [CA]) 20 September 2006 (2006-09-20) cited in the application claims 1,3-5,8 paragraphs [0016], [0017] -----	1-18

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