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(54) MICRO-SCALE FUEL CELL FIBERS AND TEXTILE STRUCTURES THEREFROM

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(57) **ABSTRACT**

A proton exchange membrane fuel cell fiber has an inner and outer electrode that is either an anode or cathode, a first and second layer that include either a fuel catalyst layer or oxidant catalyst layer, and a proton exchange membrane. These components are combined into a fiber having a diameter of about 5 mm or less and the length of about 1 cm or more.

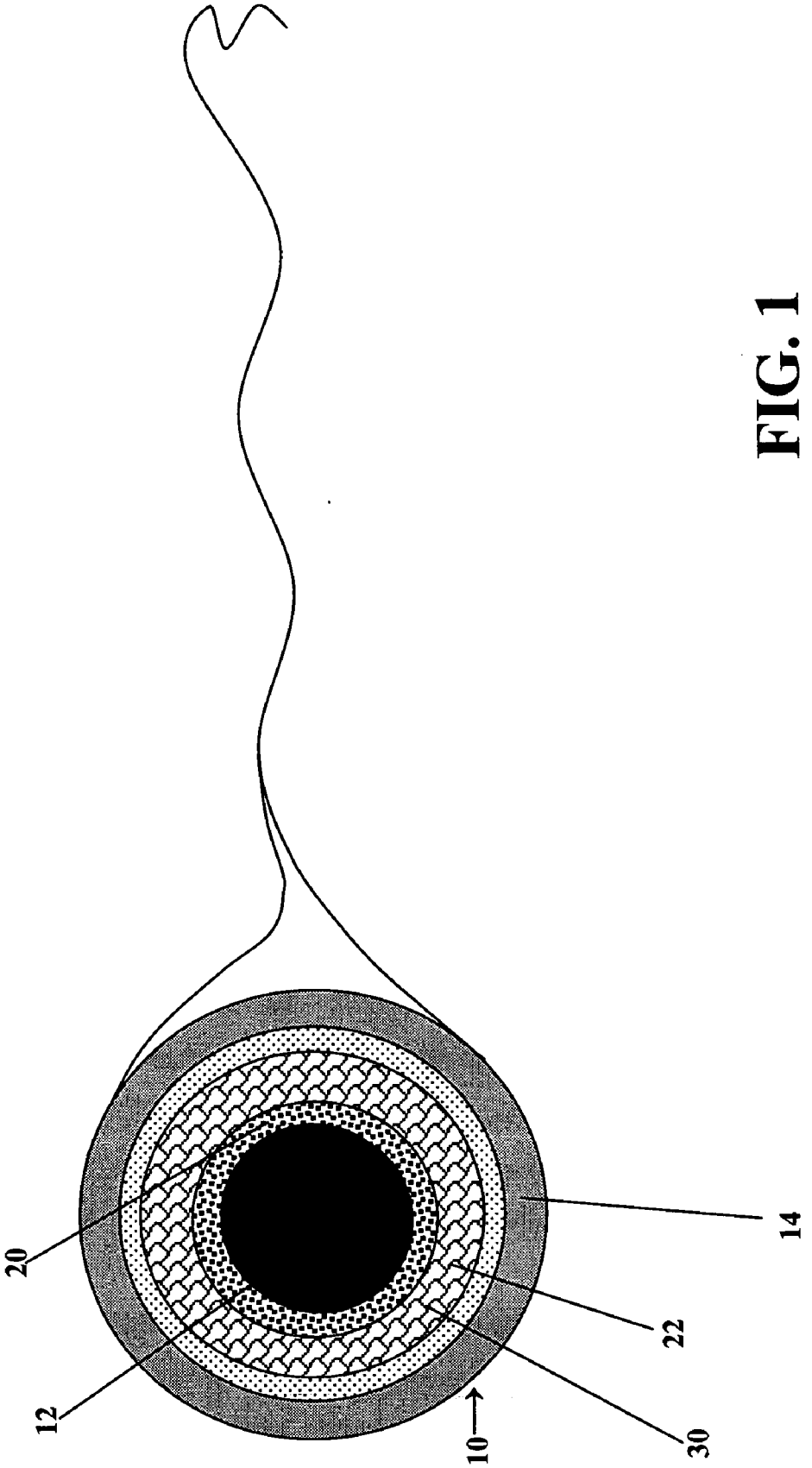

FIG. 1

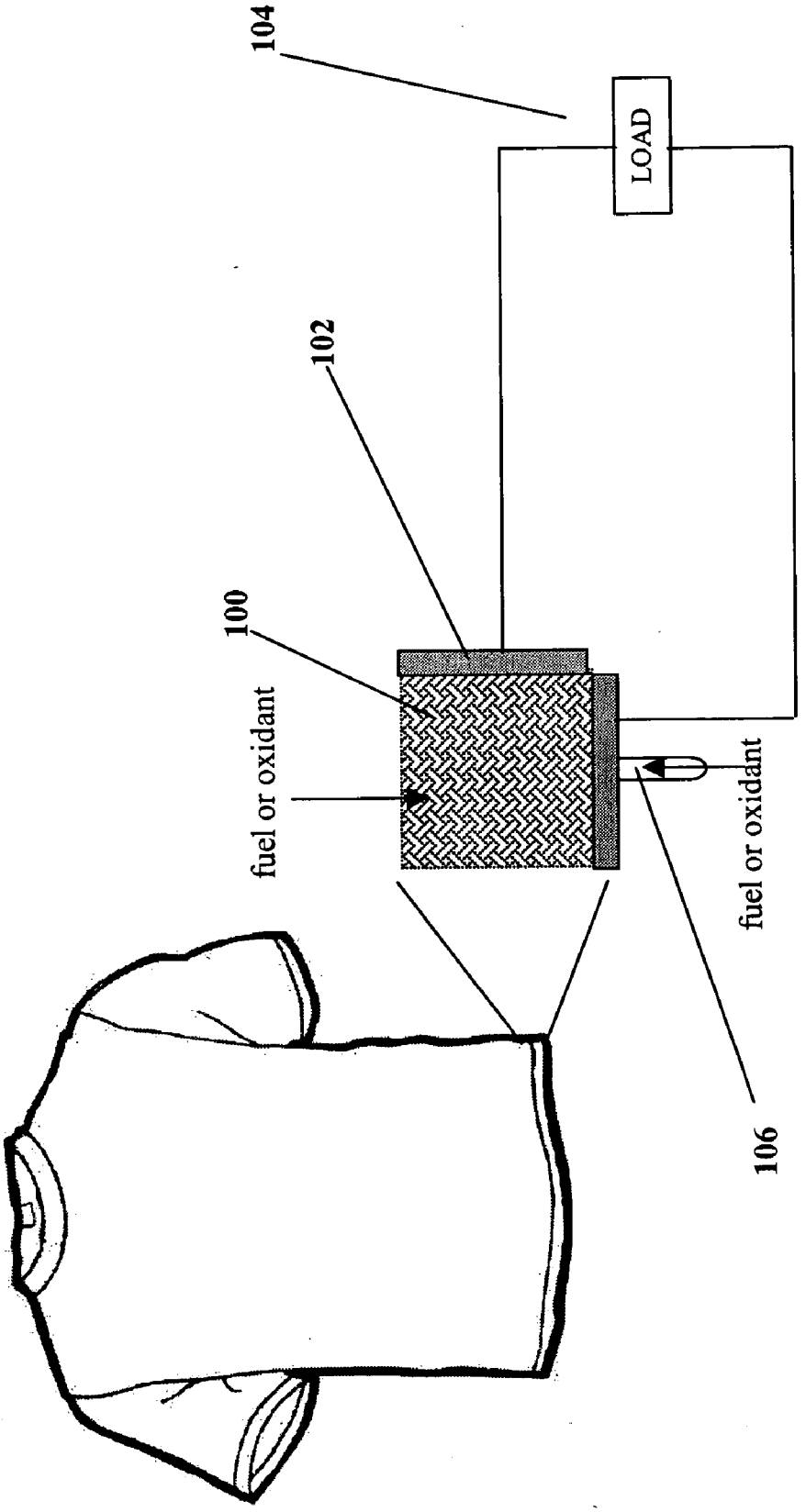

FIG. 2

MICRO-SCALE FUEL CELL FIBERS AND TEXTILE STRUCTURES THEREFROM

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] The invention described herein may be manufactured and used by or for the government of the United States of America for governmental purposes without the payment of any royalties thereon or therefore.

FIELD OF THE INVENTION

[0002] The present invention is related to fuel cell fibers useful in the manufacture of textiles.

BACKGROUND

[0003] Fuel cell power sources have been known for some time. Hydrogen fuel cells are considered a leading technology for environmentally benign electricity generation. Fuel cells combine hydrogen and oxygen without combustion to form water and produce direct current electric power. The process effectively is a reverse electrolysis. Fuel cells provide high energy efficiency and low emissions.

[0004] Efforts have been directed in the field of Proton Exchange Membrane (PEM) based fuel cells. The basis of these PEM devices is the generation of electricity through an external circuit resulting from the electrochemical oxidation of hydrogen with molecular oxygen to produce water. During this electrochemical process, the PEM selectively transports oxidized hydrogen ions (protons) from the anode (fuel electrode) to the cathode (oxidizer electrode). PEM fuel cells operate at low temperatures, produce fast transient response, and have relatively high energy density compared to other fuel cell technologies. These fuel cells typically incorporate a supply of the reactants (typically hydrogen and oxygen) into the cell, mass transport the product (water) and inert gases (nitrogen and carbon dioxide from air) through and out of the cell, electrodes to support catalyst, collect electrical charge, and dissipate heat. Electrical and thermal resistance, reactant pressures, temperatures, surface area, catalyst availability, and geometry are the main factors affecting the performance and efficiency of a fuel cell.

[0005] PEM fuel cells are traditionally created as stacks of layered devices known as Membrane Electrode Assemblies (MEA), allowing for scalable energy density. These Membrane Electrode Assemblies, generally sheet-like materials, are typically inflexible and prone to small failures that destroy the power generating ability of the whole material resulting in an inadequate basis for forming fabric. Additionally, PEM fuel cells have been developed as cylindrical PEM fuel cells.

[0006] There is a need in the art to provide convenient fuel cell sources for individual use. The present invention addresses this and other needs.

SUMMARY

[0007] The present invention includes a proton exchange membrane fuel cell fiber having an inner electrode, a first layer selected from the group consisting of a fuel catalyst layer or oxidant catalyst layer intimately adjoined to the inner electrode, an outer electrode, a second layer selected from the group consisting of a fuel catalyst layer or oxidant catalyst layer intimately adjoined to the outer electrode, and a proton exchange membrane between the first and second layers. Each of the inner and outer electrodes are exclusively one of either an anode or cathode, and the diameter of the fiber ranges from about 5 mm or less and the length ranges from about 1 cm or more.

[0008] The present invention also includes a method for producing power from electrochemical oxidation including the steps of providing the above-described proton exchange membrane fuel cell fiber and conducting an electrochemical process therein effective to produce energy.

[0009] The present invention is particularly applicable for use in textiles, such as garments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. **1** illustrates an exemplary fiber-like fuel cell; and

[0011] FIG. **2** illustrates an exemplary use of the fiber-like fuel cell of FIG. **1** in a textile.

DETAILED DESCRIPTION

[0012] The present invention provides a microscale, fiber-like, proton exchange membrane (PEM) fuel cells (referred to herein as "fiber-like fuel cells" or "fuel cell fibers") and methods for their construction. These fiber-like fuel cells provide a source of electric power through electrochemical oxidation of hydrogen or a hydrogen rich fuel. The fiber-like form can be used to weave textiles comprised entirely of fuel cell fibers or in conjunction with other natural and synthetic fibers. The textiles can be prepared in such a manner to allow for the construction of garments, coverings, or other functional textiles. Paired with an appropriate fuel source, the present invention allows for portable power available for use in personal electronics or integrated systems within the textile.

[0013] As seen in FIG. **1**, the present invention includes a fiber-like fuel cell **10** for generating electrical power through an oxidative process. Referring to FIG. **1**, the fuel cell fibers **10** include an inner (or central) electrode **12** and outer (or covering) electrode **14**. Each of the inner **12** and outer **14** electrodes are exclusively either an anode or cathode, such that an anode and cathode are both present within the invention. The inner and outer electrodes **12** and **14** may comprise either an anode or cathode, or cathode and anode, respectively, with an anode inner electrode **12** and cathode outer electrode **14** functionality preferred. The electrode **12** or **14**, when present as an anode, may include any appropriately configured conductive structure for effective liquid and gas transfer therethrough, such as fuel diffusion. The electrode **12** or **14**, when present as a cathode, may include appropriately configured conductive structure for effective liquid and gas transfer, Representative configurations of the inner and outer electrodes **12** and **14** include, for example, porous, hollow, open tubular structures, channeled, and combinations thereof. The central electrode **12**, as an anode, may be comprised of a conductive porous material. This porous material may be formed as a consolidated and flexible fiber to provide support to the additional layers of the fuel cell fibers **10**. The inner and outer electrodes **12** and **14** may include appropriate composition for use as an electrode, such as pressed carbon black, pressed graphite,

continuous carbon fiber, nanostructured conductive oxide (e.g., ruthenium oxide, iridium oxide), ceramic or polymer fiber-based thin conductive films, ceramic or polymer fiber-based thin metallic films, porous metal wire, porous conductive polymers, porous composites thereof, and/or combinations thereof, and the like. The electrodes may be resistant to corrosion, provide excellent electrical conductivity, and enable fast permeation of oxygen at the cathode and hydrogen at the anode. The electrodes **12** and **14** may comprise a thickness of from about 0.001 mm to about 3 mm, such as 1 mm. The outer electrode typically is a material selected from the group consisting of vapor deposited carbon, conductive adhesive, vapor deposited metal film, conductive polymeric coating, and combinations thereof. Methodologies for the formation of the electrodes **12** and **14** may include dip coating, vapor phase, spin coating, film casting, press forming, doctor blading, and the like, and combinations thereof. For example, the outer electrode **14**, applied after the second catalyst layer is applied, may be applied through dip coating or vapor phase techniques, such as the attachment of conductive particles from the coating solution or the formation of a continuous conductive film onto the outer electrode layer **14**.

[**0014**] The electrodes **12** and **14** provide a support for the fuel catalyst layer and oxidant catalyst layer. Adjacent to the inner electrode **12**, a first layer **20** is formed. Additionally, adjacent to the outer layer, a second layer **22** is formed. These two layers **20** and **22** provide a fuel catalyst layer adjacent to the anode and an oxidant catalyst layer adjacent to the cathode of the fuel cell fiber **10** of the present invention. In an embodiment where the inner electrode **12** comprises an anode (i.e., the outer electrode comprises a cathode), the first layer **20** and second layer **22** comprise the fuel catalyst layer and oxidant catalyst layer, respectively.

[**0015**] In one embodiment of an inner anode electrode, the first layer **20**, being adjacent to the inner anode inner electrode **12**, is intimately adjoined to the inner anode electrode **12**. Additionally, the second layer **22**, adjacent to the outer cathode electrode **14**, comprises the oxidant catalyst layer.

[**0016**] In another embodiment where the inner electrode **12** comprises a cathode (i.e., the outer electrode comprises an anode), the first layer **20** and second layer **22** comprise an oxidant catalyst layer and fuel catalyst layer, respectively.

[**0017**] In both configurations, these layers are intimately adjoined to the adjacent inner or outer electrode, as applicable, and supported thereby. The catalyst layers **20** and **22** (both fuel and oxidation) may be applied by drawing the central electrode through a solution of dispersed catalytic particles (dip coating). The particles would then become dispersed on the surface of the electrode **12** and **14** and fixed upon drying. The solution for dip coating may be colloidal in nature or may involve sol-gel formation. The dip coating solution may also contain dispersed or solubilized components to assist in conduction of electricity, including similar materials that are used in the adjacent electrode. Subsequent heat treatment steps may also be used to fix the catalyst particles and/or coating. Alternatively, sputtering or other vapor phase deposition techniques (e.g., rf magnetron sputtering, ion beam sputtering, electron beam sputtering, chemical vapor deposition,) may be used for the application of the layers **20** and **22**, with the catalytic particles built up from energetic molecular or atomic vapor.

[**0018**] The fuel catalyst layer, composing either the first layer **20** or second layer **22**, comprises an appropriate fuel cell catalyst material, such as finely structured transition metals, polypeptide enzyme, metal-centered macromolecule and combinations thereof. Preferably, the fuel catalyst layer comprises finely structured transition metals. Representative catalysts include noble metal catalysts, such as platinum, gold, silver, palladium, ruthenium, rhodium, and iridium, with a preferred catalyst being platinum based. The diameter of the fuel catalyst layer may range from about 0.00001 mm to about 1 mm, 0.001 mm and may range, for example, from about 0.0001 mm to about 0.001 mm.

[**0019**] The oxidant catalyst layer, similar to the fuel catalyst layer, may comprise an appropriate catalyst material for activation of the oxidant, such as finely structured transition metals, polypeptide enzyme, metal-centered macromolecule and combinations thereof. Preferably, the oxidant catalyst layer comprises finely structured transition metals. Representative catalysts include noble metal catalysts, such as platinum, gold, silver, palladium, ruthenium, rhodium, and iridium, with a preferred catalyst being platinum based. The diameter of the oxidation layer may range from about 0.00001 mm to about 1 mm, and may range, for example from about 0.0001 mm to about 0.001 mm.

[**0020**] As further shown in FIG. **1**, a proton exchange membrane **30** is placed between the first **20** and second **22** layers, away from the electrodes **12** and **14**. The proton exchange membrane **30** may comprise a proton conductive polymer or continuous inorganic film, and may includes Nafion®. Nafion® is a fluorinated organic polymer having multiple pendant sulfonic acid groups. Nafion® is produced by and a trademark of E.I. Du Pont de Nemours & Co. Inc. of Wilmington, Del., for a commercially polysulfonated membrane or solution. Nafion® has a chemical structure of $—(CF_2CF_2)_n—CF_2C(F—)—(OCF_2CF(CF_3)—)OCF_2SO_3H$; a copolymer of polytetrafluoroethane and polysulfonylfluoride vinyl ether having about one in eight monomer units is sulfonated. Nafion® is available from Solution Technology, Inc. of Philadelphia, Pa.

[**0021**] The proton exchange membrane (PEM) **30**, may be applied in a similar fashion as the catalyst layer. A solution of the dissolved PEM reactant or precursor may be applied by dip coating when the catalyst coated flexible inner electrode **12** is drawn slowly from a solution and allowed to dry, allowing a thin polymer coating to form constituting the PEM. Several repetitions of this dip coating may be required for optimizing proton conduction behavior of the final fuel cell. The drying step may use controlled drying through temperature and humidity adjustment.

[**0022**] The proton exchange membrane may be treated with various chemicals to adjust proton conduction behavior. This includes peroxides, mineral acids, organic acids, water and other such compounds known in the art for adjusting proton conduction behavior.

[**0023**] The fiber-like fuel cell **10** has a diameter of the fiber that may range from about 5 mm or less and a length of from about 1 cm or more. These dimensions allow for the use of the fiber-like fuel cells **10** to be woven together into a fabric, and is particularly applicable for the manufacture of textiles, such as garments. The small diameter also facilitates high surface area interactions for activation of the fuel and oxidant sources.

[0024] The fuel cell fiber **10** produces power from electrochemical oxidation of fuel hydrogen when an oxidative process is conducted through it to effectively produce energy. Electricity, through conversion of hydrogen or a hydrogen-rich fuel into water, through electrochemical oxidation is created in a manner that provides an inherently small form factor that can be scaled to allow batteries or other energy cells to be constructed. In operation, the porous anode allows diffusion of hydrogen gas from the fuel source side of the anode to the catalyst layer. Alternately, miniature flow channels, or other similar device for transporting the fuel may be used. Preferably, the fuel source, e.g., hydrogen gas (H_2), is channeled within the textile to and/or through the fiber-like fuel cells. As hydrogen gas fuel passes through the anode and contacts the fuel catalyst layer, the hydrogen gas molecules decompose into hydrogen atoms (H^+) separated from their electrons (e^-). A continuous flow of these hydrogen ions pass through the PEM, contacting an active oxidant, e.g., reduced oxygen, in the oxidation layer. In the example of oxidation with oxygen, oxygen molecules fed through the cathode layer are broken down within the oxidant catalyst layer into oxygen atoms, which accept the electrons that were stripped from the hydrogen atoms and react with the hydrogen ions, forming water. The electrodes **12** and **14** of the present invention act to conduct electricity, providing a current pathway in the complete fuel cell.

[0025] As seen in FIG. **2**, the fuel cell fibers **10** are assembled into a textile because of their flexible and thread-like in nature, e.g., the relatively long continuous fuel cell fibers are woven to form fabrics and/or garments **100**. In one particular embodiment, the garments possess special termination of the fiber ends in pressure sealable seams **102**, with the seams **102** having channels for flowing fuel gas from a storage system or fuel generation system, such as, methanol reformer, metal hydrides, or borohydride salts **106**. As the gas is flowed into the core electrode (anode) from these seams **102**, oxidant gas is also provided by air flow over and through the woven fabric **100**.

[0026] One possible alternative operation of the present invention includes the oxidant, such as oxygen or ambient air, flowed into the seams **102** and subsequently into the core (cathode) electrodes. In this embodiment, the fabric **100** itself is bathed in fuel gas from a storage system or from a generation system (e.g., methane reforming coatings). The fuel cell fibers within the textile **100** generate current flow **104**, through an external load bearing circuit through electrical contacts made at the termination seams. The electrical contact results from processing of the fiber coating with leader segments of both the core electrode and the outer electrode layer created at the front and end of the fiber, respectively.

[0027] Conventional portable and integrated electronics rely on separate battery cells to provide required electric power. Use of the fiber-like fuel cells **10** of the present invention allows for a fabric power source that can be incorporated into devices integrated into the fabric material, such as a housing or covering. Such fabrics may also be packaged as traditional batteries for drop-in replacement scenarios. Additionally, the fuel cell fiber materials of the present invention allow for defects in individual fibers without destroying the power generating capacity of the entire textile. The woven nature of the material constructed from fuel cell fibers **10** allows sufficient flexibility for garment or structure covering construction. A woven product composed partially or totally of the fiber-like fuel cells may be substituted for other woven goods, providing applications such as powering wearable computers and instrumentation, incorporation medical and health montoring devices into advanced integrated garments, special feature garments having advanced electronic integrated systems such as color changing and temperature modification, and the like. Additionally, sheets of fuel cell fabric may be used to construct light weight, larger scale fuel cells for battery replacement and electric power generation plants.

EXAMPLE 1

General Construction

[0028] A thin fiber-like PEM fuel cell is manufactured to contain the fuel cell layers of a current collecting electrode (anode) that is porous in nature to allow fuel diffusion throughout and including the interface with the fuel catalyst layer, a fuel catalyst layer comprised of catalyst materials in intimate contact with the fuel electrode and the proton exchange membrane, a Nafion® proton exchange membrane in intimate contact with both the fuel and oxidation layer or catalysts, an oxidation catalyst that is in intimate contact with the proton exchange membrane and the cathode, and a cathode that is porous in nature to allow oxygen or another oxidizing compound to freely flow throughout and including the interface with the oxidation catalyst layer. The total diameter of the fiber is less than 5 mm to facilitate weaving operations to form textiles.

EXAMPLE 2

Specific Construction

[0029] A fuel cell is constructed with a poly(acrylonitrile) fiber that has been blended with sacrificial organic solids. This fiber is then heated to 300° C. in an oven in air until the fiber has oxidized. The fiber is then treated at 1500° C. to complete carbonization. The fiber loses the sacrifical organic solids and is now a porous carbon fiber with significant conductivity (1×10^5 S/m). The carbon fiber is the basis of the inner electrode. The fuel catalyst layer is formed by mixing a 20 wt % solution of Nafion® with a platinum salt such as $PtCl_2$ in water and alcohols. The quantity of platinum is adjusted so that the final platinum distribution is 0.1-0.2 mg/cm^2. The working fiber is slowly drawn through a solution. The dip-coated layer is then dried at 150-200° C. to form the fuel catalyst layer. The proton exchange membrane is formed from a 20 wt % solution of Nafion® through several repeated dip coating sessions. The membrane is converted to its sodium salt using standard methods for heat processing. This is then dried at 150° C. to form the final membrane layer. The oxidant catalyst layer is then formed through the same technique described for the fuel catalyst layer. The membrane is then converted to fully protonated form (acidified) through treatment of the entire fiber in a sulfuric acid solution. The outer electrode is then formed through dip coating the fiber in a viscous dispersion of conductive carbon aerogel powder in 20 wt % Nafion® and a glycerol. This is dried to produce a delicate dispersion of the powder on the surface. This is then consolidated and made hydrophobic through the chemical vapor deposition of hexafluoropropylene oxide to form poly(tetrafluoroethylene) binding structure. The consolidated outer layer is the

porous and conductive outer electrode with sufficient hydrophobicity to exclude the product water for evaporation and cooling of the fuel cell fiber.

[0030] The foregoing summary, description, and examples of the present invention are not intended to be limiting, but are only exemplary of the inventive features, which are defined in the claims.

What is claimed is:

1. A proton exchange membrane fuel cell fiber, comprising:

an inner electrode;

a first layer selected from the group consisting of a fuel catalyst layer and oxidant catalyst layer intimately adjoined to the inner electrode;

an outer electrode;

a second layer selected from the group consisting of a fuel catalyst layer and oxidant catalyst layer intimately adjoined to the outer electrode; and,

a proton exchange membrane between the first and second layers,

wherein each of the inner and outer electrodes are exclusively one of either an anode or cathode, and,

wherein the diameter of the fiber ranges from about 5 mm or less and the length ranges from about 1 cm or more.

2. The fiber of claim 1, wherein the inner electrode comprises a conductive structure effective for liquid or gas transfer therethrough selected from the group consisting of porous, hollow, open tubular and combination thereof.

3. The fiber of claim 1, wherein the inner electrode comprises an anode and the outer electrode comprises a cathode.

4. The fiber of claim 1, wherein the inner electrode comprises a cathode and the outer electrode comprises an anode.

5. The fiber of claim 1, wherein the inner and outer electrodes independently comprise a composition selected from the group consisting of pressed carbon black, pressed graphite, continuous carbon fiber, nanostructured conductive oxide, ceramic or polymer fiber-based thin conductive films, ceramic or polymer fiber-based thin metallic films, porous metal wire, porous conductive polymers, or combinations thereof.

6. The fiber of claim 1, wherein the fuel catalyst layer comprises a catalyst material selected from the group consisting of finely structured transition metals, polypeptide enzyme, metal-centered macromolecule and combinations thereof.

7. The fiber of claim 6, wherein the fuel catalyst layer comprises finely structured transition metals.

8. The fiber of claim 1, wherein the proton exchange membrane comprises a proton conductive polymer or continuous inorganic film.

9. The fiber of claim 8, wherein the proton exchange membrane comprises a chemical structure of $—(CF_2CF_2)_n—CF_2C(F—)—(OCF_2CF(CF_3)—)OCF_2SO_3H$.

10. The fiber of claim 1, wherein the oxidant catalyst layer comprises a catalyst material selected from the group consisting of finely structured transition metals, polypeptide enzyme, metal-centered macromolecule and combinations thereof.

11. The fiber of claim 10, wherein the oxidant catalyst layer comprises a finely structured transition metals.

12. The fiber of claim 1, wherein the outer electrode is a material selected from the group consisting of vapor deposited carbon, conductive adhesive, vapor deposited metal film, conductive polymeric coating, liquid deposited carbon black, liquid deposited graphite, liquid deposited metal particles and combinations thereof.

13. A textile comprising the fiber of claim 1.

14. The textile of claim 13, wherein the textile is substantially comprised of the fiber of claim 1.

15. A garment comprising the textile of claim 13.

16. A method for producing power from electrochemical oxidation, comprising the steps of:

providing a proton exchange membrane fuel cell fiber having an inner electrode, a first layer selected from the group consisting of a fuel catalyst layer and oxidant catalyst layer intimately adjoined to the inner electrode, an outer electrode, a second layer selected from the group consisting of a fuel catalyst layer and oxidant catalyst layer intimately adjoined to the outer electrode and a proton exchange membrane between the first and second layers, wherein each of the inner and outer electrodes are exclusively one of either an anode or cathode and wherein the diameter of the fiber ranges from about 5 mm or less and the length ranges from about 1 cm or more; and,

conducting an oxidative process therein effective to produce energy.

17. The method of claim 16, further comprising the step of channeling a fuel source to the fiber.

18. The method of claim 16, wherein the inner electrode comprises an anode.

19. The method of claim 16, wherein the inner electrode comprises a cathode.

20. The method of claim 18, wherein the step of adjoining the cathode comprises a method selected from the group consisting of dip coating, vapor phase, spin coating, film casting, press forming, doctor blading, and combinations thereof.

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