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(54) **FUEL CELL ELECTRODES WITH TRIAZOLE MODIFIED POLYMERS AND MEMBRANE ELECTRODE ASSEMBLIES INCORPORATING SAME**

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Related U.S. Application Data

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(51) **Int. Cl.**

H01M 4/86 (2006.01)
H01M 4/88 (2006.01)

(Continued)

(52) **U.S. Cl.**

CPC ***H01M 4/8807*** (2013.01); ***H01M 4/8668*** (2013.01); ***H01M 4/8828*** (2013.01); ***H01M 4/92*** (2013.01); ***H01M 8/1004*** (2013.01); *H01M 2008/1095* (2013.01); *Y02E 60/521* (2013.01)

(58) **Field of Classification Search**

CPC H01M 4/8668
USPC 429/400–535
See application file for complete search history.

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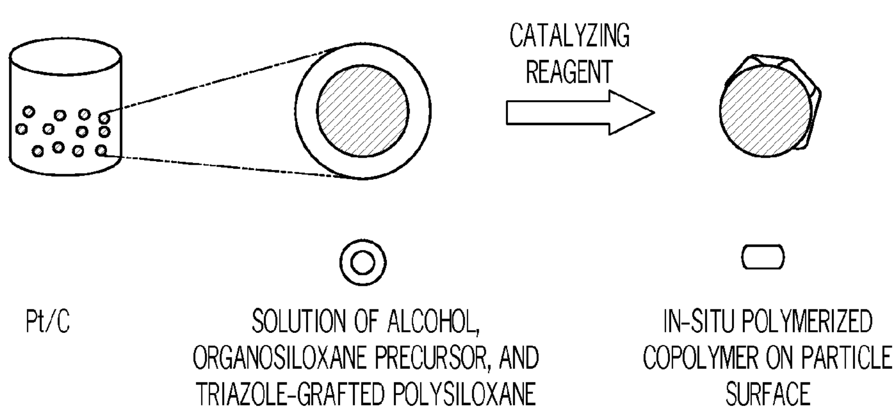
Primary Examiner — Jonathan G Leong
(74) *Attorney, Agent, or Firm* — Dinsmore & Shohl LLP

(57) **ABSTRACT**

Embodiments of the present anhydrous fuel cell electrodes comprise an anhydrous catalyst layer and a gas diffusion layer, wherein the anhydrous catalyst layer comprises at least one catalyst, about 5 mg/cm^2 to about 100 mg/cm^2 of phosphoric acid added as a catalyzing reagent during formation of the catalyst layer, and a binder comprising at least one triazole modified polymer, wherein the triazole modified polymer comprises a polysiloxane backbone and a triazole substituent.

20 Claims, 9 Drawing Sheets



(51) **Int. Cl.**
H01M 4/92 (2006.01)
H01M 8/10 (2006.01)

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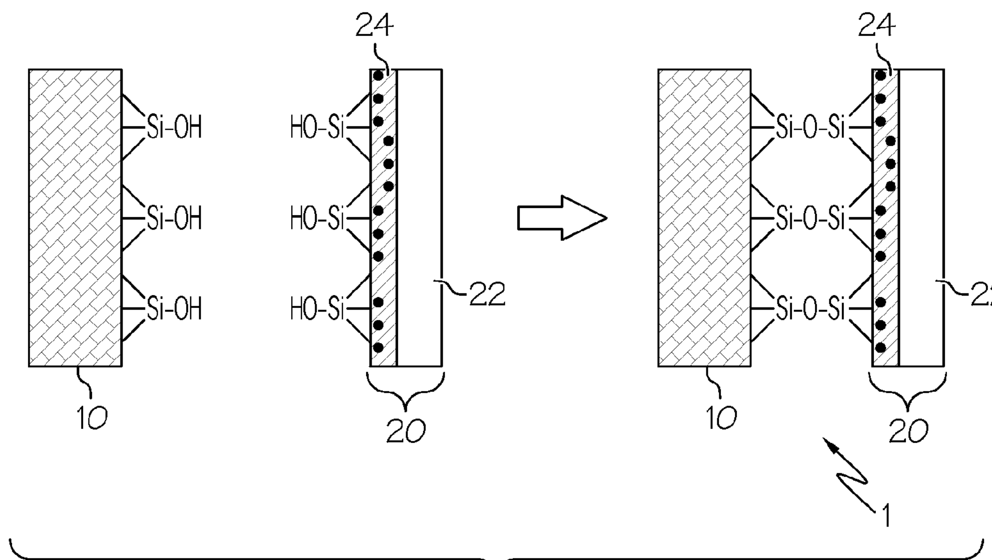

24
Si-OH
Si-OH
Si-OH
HO-Si
HO-Si
HO-Si
22
10
20
24
Si-O-Si
Si-O-Si
Si-O-Si
22
10
20
1

FIG. 1

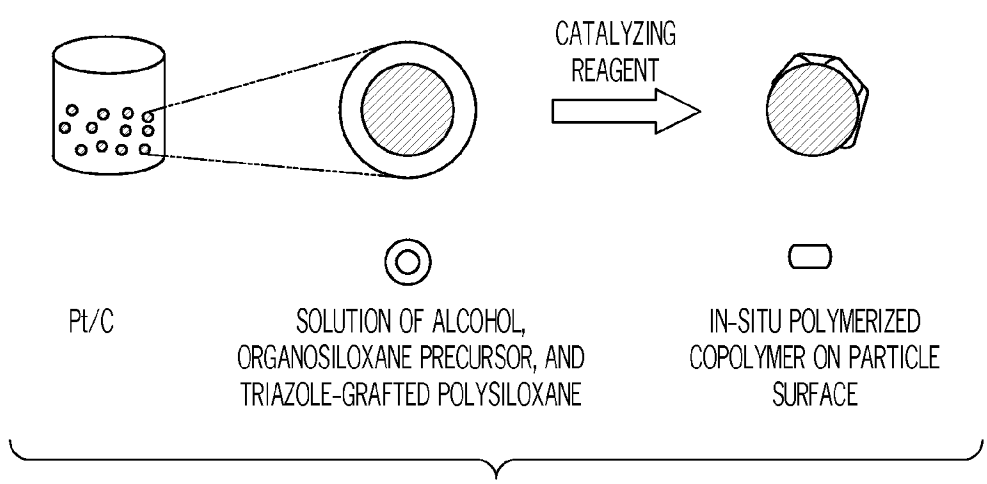

CATALYZING REAGENT
Pt/C
SOLUTION OF ALCOHOL, ORGANOSILOXANE PRECURSOR, AND TRIAZOLE-GRAFTED POLYSILOXANE
IN-SITU POLYMERIZED COPOLYMER ON PARTICLE SURFACE

FIG. 2

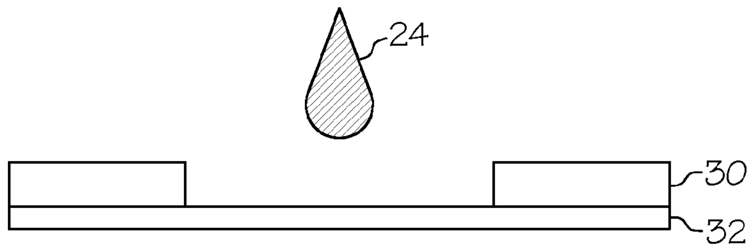


FIG. 3A

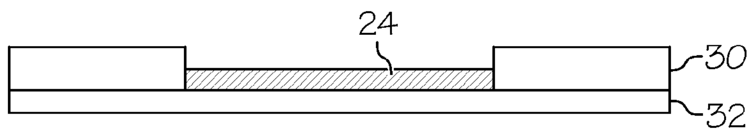


FIG. 3B

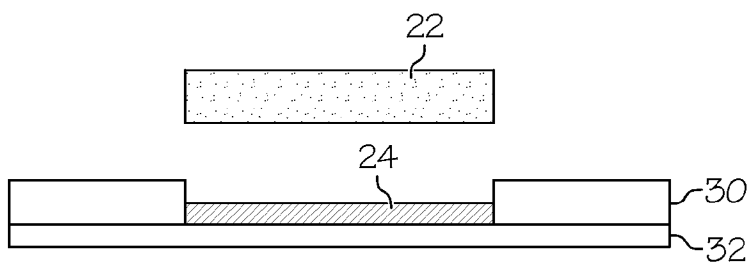


FIG. 3C

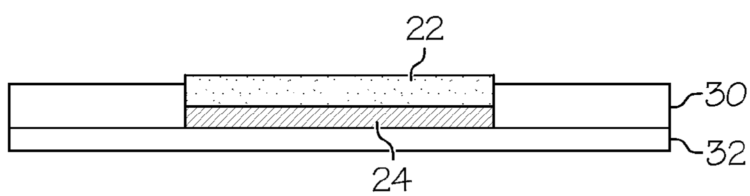


FIG. 3D

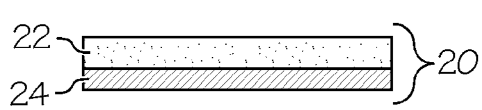


FIG. 3E

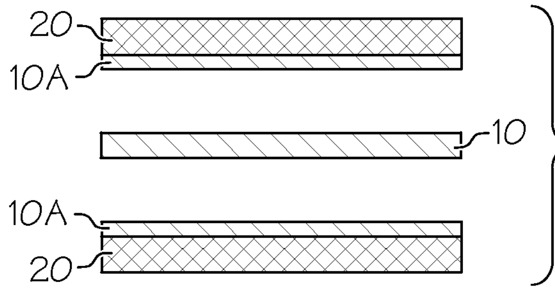


FIG. 4A

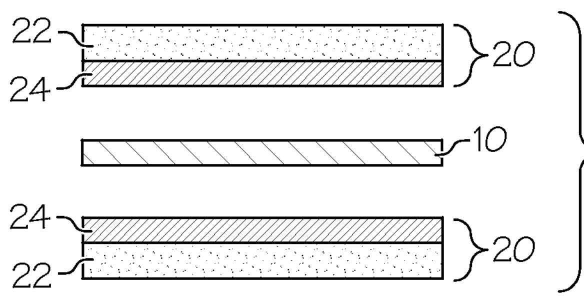


FIG. 4B

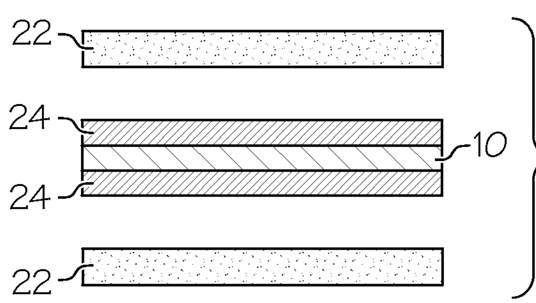


FIG. 4C

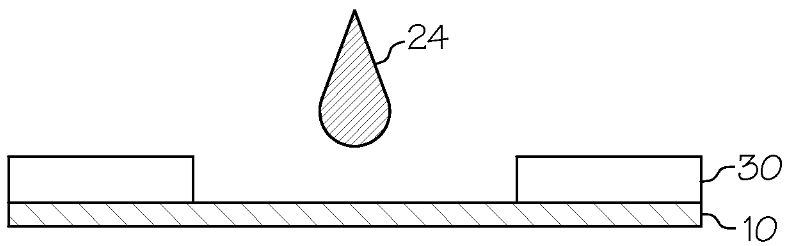


FIG. 5A

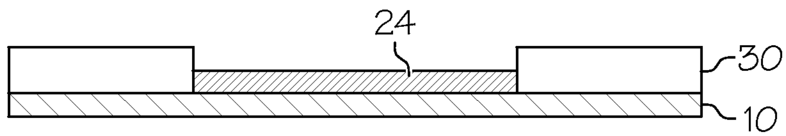


FIG. 5B

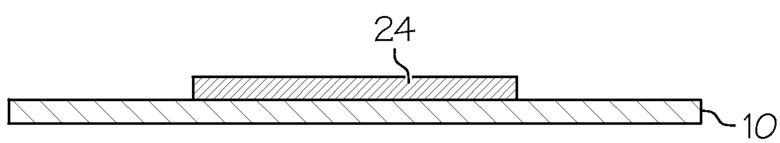


FIG. 5C

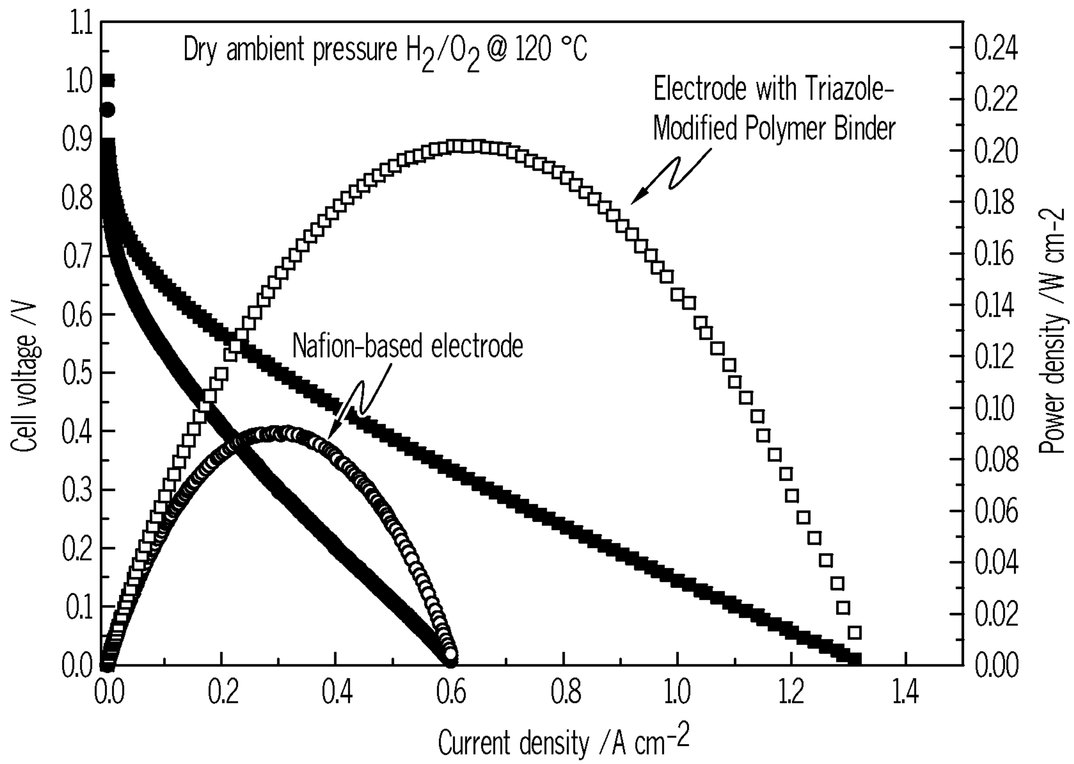

Dry ambient pressure H2/O2 @ 120 °C
Electrode with Triazole-Modified Polymer Binder
Nafion-based electrode
Cell voltage /V
Power density /W cm-2
Current density /A cm-2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

FIG. 6

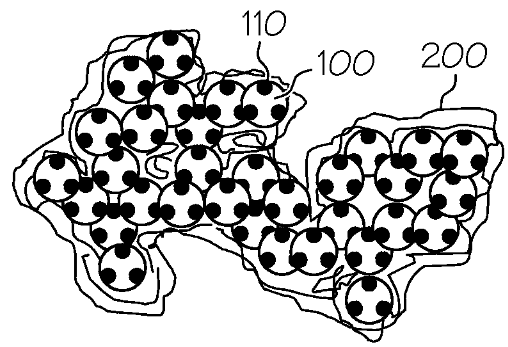


FIG. 7A

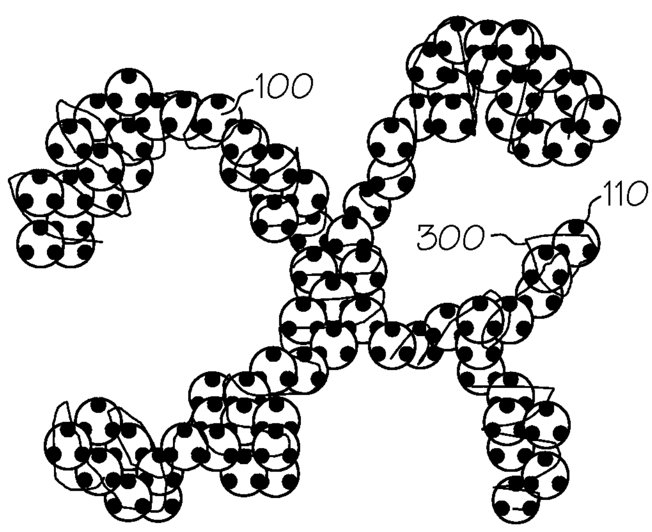


FIG. 7B

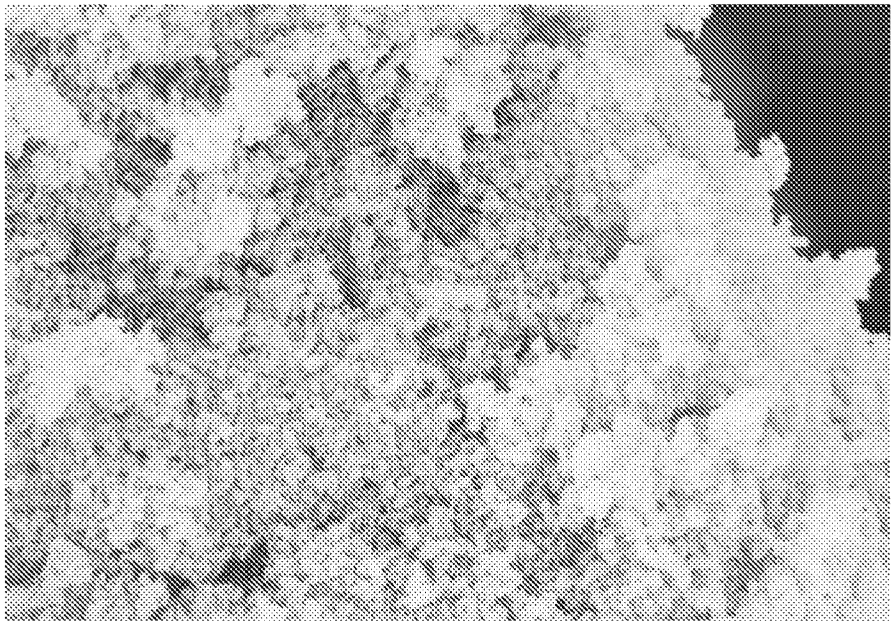


FIG. 8A

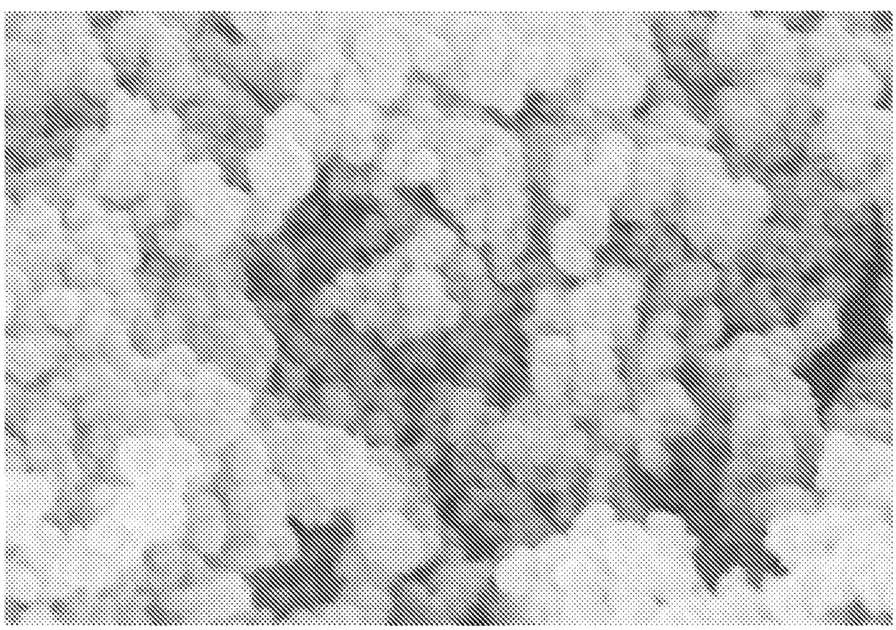


FIG. 8B

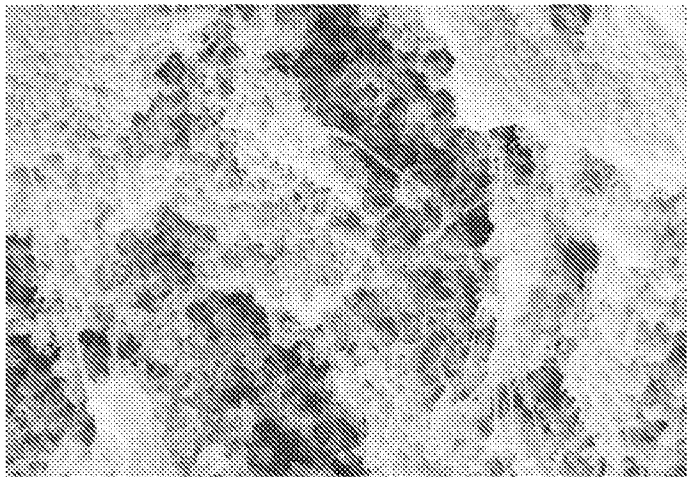


FIG. 9A

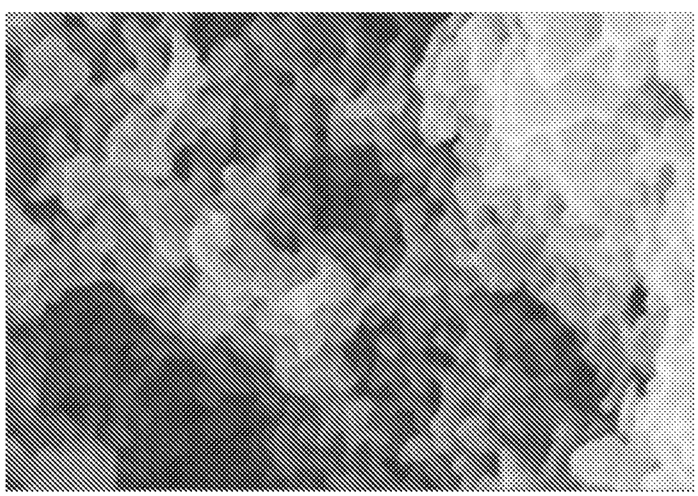


FIG. 9B

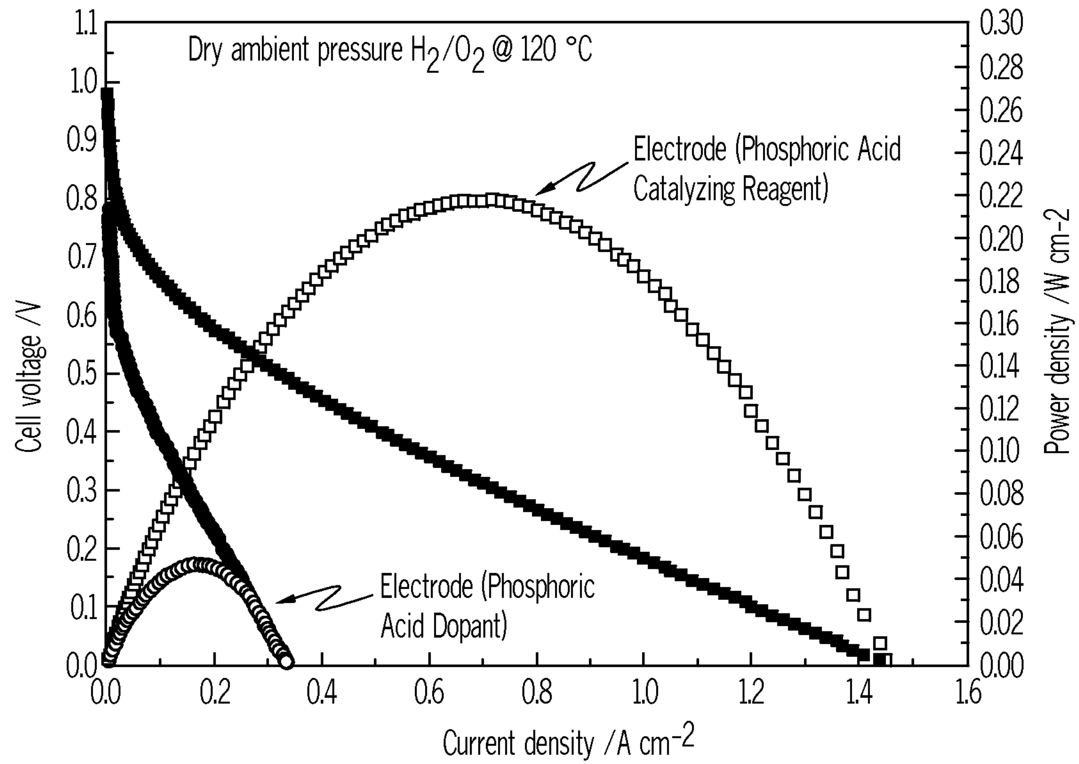

Dry ambient pressure H_2/O_2 @ 120 °C
Electrode (Phosphoric Acid Catalyzing Reagent)
Electrode (Phosphoric Acid Dopant)
Cell voltage /V
Power density /W cm-2
Current density /A cm^{-2}
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6

FIG. 10

FUEL CELL ELECTRODES WITH TRIAZOLE MODIFIED POLYMERS AND MEMBRANE ELECTRODE ASSEMBLIES INCORPORATING SAME

CROSS-REFERENCE TO RELATED APPLICATION

This application is a divisional application of U.S. patent application Ser. No. 12/196,452 filed Aug. 22, 2008, which is incorporated by reference herein in its entirety.

TECHNICAL FIELD

Embodiments of the present invention are generally directed to electrodes for membrane electrode assemblies in proton electrolyte membrane fuel cells (PEMFC), and are specifically directed to electrodes having catalyst layers comprising triazole modified polymers and phosphoric acid which facilitates operability at higher temperatures (e.g., 120° C. and higher).

BACKGROUND

In an effort to find new energy sources, fuel cells using an electrochemical reaction to generate electricity are becoming an attractive energy alternative. Fuel cells offer low emissions, high fuel energy, high conversion efficiencies, and low levels of noise and vibration. Proton electrolyte membrane fuel cells (PEMFCs) have been identified in many industries, such as the automotive industry, as an especially advantageous fuel cell design, and therefore, the development of new and improved materials and components inside the PEMFC is ongoing.

In particular, high temperature PEMFCs operational above 120° C. with low humidification or without humidification, can offer several advantages such as anode tolerance to significant quantities of carbon monoxide poisoning, operability without humidification, electrode kinetics enhanced by high temperatures (e.g. 120° C.), elimination of cathode flooding, and ease of thermal management. While conventional electrodes for PEMFCs are mainly focused on Nafion®-based electrodes (e.g., commercial E-TEK® electrodes), Nafion®-based electrodes are only operable for low temperature PEMFCs (e.g., operational below 100° C.), and are reliant on external or internal (e.g., self-humidifying) humidity for proton transfer.

Due to the issues with Nafion®-based electrodes, alternative polymers which facilitate operation at high temperature without humidity have been studied. For example, a blend of polybenzimidazole (PBI) and phosphoric acid has been identified as a feasible composition for operation at high temperatures. The blend of PBI and phosphoric acid performs the function that water provides in Nafion®-based electrodes (i.e., proton transfer), thus humidification is not necessary. However, to achieve acceptable proton transfer and conductivity, the PBI/phosphoric acid blend requires substantial amounts of phosphoric acid (e.g., 3.5 to 7.5 H_3PO_4 per PBI repeating unit), which results in acid leeching and corrosion of the membrane electrode assembly. As a result, improved compositions for catalyst layers of fuel cell electrodes that maximize proton transfer and conductivity while minimizing corrosion is highly desirable.

SUMMARY

Embodiments of the present invention are directed to catalyst layers of fuel cell electrodes that are operable at high temperatures without humidification, and membrane electrode assemblies which incorporate these fuel cell electrodes.

According to one embodiment, an anhydrous fuel cell electrode comprising an anhydrous catalyst layer and a gas diffusion layer is provided. The anhydrous catalyst layer comprises at least one catalyst, about 5 mg/cm^2 to about 100 mg/cm^2 of phosphoric acid added as a catalyzing reagent during formation of the catalyst layer, and a binder comprising at least one triazole modified polymer, wherein the triazole modified polymer comprises a polysiloxane backbone and a triazole substituent. According to a further embodiment, the catalyst comprises platinum.

According to yet another embodiment, a proton electrolyte membrane fuel cell comprising an electrolyte membrane, and a pair of fuel cell electrodes comprising an anhydrous catalyst layer and a gas diffusion layer is provided. The anhydrous catalyst layer comprises at least one catalyst, about 5 mg/cm^2 to about 100 mg/cm^2 of phosphoric acid added as a catalyzing reagent during formation of the catalyst layer, and a binder comprising at least one triazole modified polymer, wherein the triazole modified polymer comprises a polysiloxane backbone and a triazole substituent.

These and additional features provided by the embodiments of the present invention will be more fully understood in view of the following detailed description, in conjunction with the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

The following detailed description of specific embodiments of the present invention can be better understood when read in conjunction with the drawings enclosed herewith.

FIG. **1** is a schematic view of the components of a membrane electrode assembly according to one or more embodiments of the present invention;

FIG. **2** is a schematic view illustrating the reaction mechanism for the catalyst layer of the fuel cell electrode according to one or more embodiments of the present invention;

FIGS. **3**A-**3**E are schematic views illustrating a method of producing a fuel cell electrode according to one or more embodiments of the present invention;

FIGS. **4**A-**4**C are schematic views illustrating a method of producing a membrane electrode assembly according to one or more embodiments of the present invention;

FIGS. **5**A-**5**C are schematic views illustrating a method of applying a catalyst ink to a surface of a membrane according to one or more embodiments of the present invention;

FIG. **6** is a graphical illustration comparing the MEA performance of Nafion®-based electrodes to an electrode including a catalyst layer with a triazole modified polymer according to one or more embodiments of the present invention;

FIG. **7**A is a schematic view illustrating the microstructure of a catalyst layer produced by adding phosphoric acid as a dopant after the formation of the catalyst layer according to one or more embodiments of the present invention;

FIG. **7**B is a schematic view illustrating the microstructure of a catalyst layer produced by adding phosphoric acid as a catalyst reagent during the formation of the catalyst layer according to one or more embodiments of the present invention;

FIGS. **8**A and **8**B are scanning electron micrograph (SEM) images with 2 μm and 200 nm magnification, respectively, of the microstructure of a catalyst layer produced by adding phosphoric acid as a dopant after the formation of the catalyst layer according to one or more embodiments of the present invention;

FIGS. **9**A and **9**B are scanning electron micrograph (SEM) images with 2 μm and 200 nm magnification, respectively, of the microstructure of a catalyst layer produced by adding phosphoric acid as a catalyst reagent during the formation of the catalyst layer according to one or more embodiments of the present invention; and

FIG. **10** is a graphical illustration comparing the MEA performance of an electrode having a phosphoric acid doped catalyst layer to an electrode having a phosphoric acid catalyzed catalyst layer according to one or more embodiments of the present invention.

The embodiments set forth in the drawings are illustrative in nature and not intended to be limiting of the invention defined by the claims. Moreover, individual features of the drawings and invention will be more fully apparent and understood in view of the detailed description.

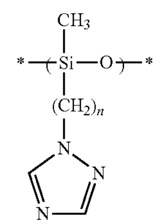
DETAILED DESCRIPTION

Embodiments of the present invention are generally directed to membrane electrode assemblies in proton electrolyte membrane fuel cells (PEMFC), and are specifically directed to membrane electrode assemblies comprising catalyst layers with triazole modified polymeric binders which facilitate operability at higher temperatures (e.g., 120° C. and higher).

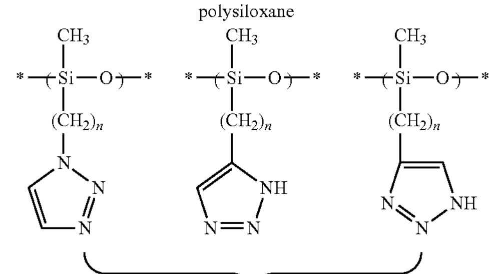
Referring to FIGS. **1** and **4**B, a membrane electrode assembly **1** may comprise an electrolyte membrane **10**, and a pair of fuel cell electrodes **20** (e.g., gas diffusion electrodes) disposed on opposite sides of the electrolyte membrane **10**. As would be familiar to one of ordinary skill in the art, the pair of electrodes **20** is the anode and cathode of the membrane electrode assembly **1**. Each electrode **20** (e.g., anode or cathode) comprises a catalyst layer **24** and a gas diffusion layer **22**. As shown in FIGS. **4**B and **4**C, the catalyst layer **24** of each electrode **20** is coupled to opposite surfaces of the electrolyte membrane **10**. Referring to FIG. **4**A, it is also contemplated that an electrolyte primer layer **10**A, which may comprise the same composition as the electrolyte membrane **10**, may be applied to the electrode to improve adhesion between the electrode **20** and the electrolyte membrane **10**. The catalyst layer **24** may comprise at least one catalyst, phosphoric acid, and a binder. The catalyst may comprise many suitable compositions, for example, platinum, platinum alloys, carbon, or electrically conductive materials and combinations thereof. In one embodiment, the catalyst may comprise a mixture of platinum and carbon, for example, 20 to 60 wt % Pt on a carbon support. In some embodiments, the Pt may comprise a loading amount ranging from about 0.2 to about 4 mg/cm^2. The Pt catalyst can be one that is commercially available, such as E-TEK® brand Pt manufactured by BASF Fuel Cell, and the C support may be carbon black VULCAN® XC72 produced by Cabot Corp. Additional catalyst compositions (e.g., rhodium or palladium) are also contemplated herein.

In addition, the catalyst layer may also comprise phosphoric acid. The phosphoric acid may act to increase the proton transfer and conductivity inside the catalyst layer (similar to the binder discussed below). In one embodiment, the phosphoric acid may be added as a catalyzing reagent during the formation of the catalyst layer as shown in FIG. **2**. Alternatively, the phosphoric acid may be added as a dopant after the catalyst layer has been formed. In exemplary embodiments, the phosphoric acid may be loaded in an amount ranging from about 5 to about 100 mg/cm^2, from about 10 mg/cm^2 to about 20 mg/cm^2, or in another suitable amount familiar to one of ordinary skill in the art. As will be described in greater detail below, adding phosphoric acid as a catalyzing reagent improves the morphology and the final properties of the catalyst layer. However, it should be understood that although this description focuses on the use of phosphoric acid, other acids or acid/base combinations are also contemplated herein for use as a catalyzing reagent.

In one embodiment, the binder may comprise at least one triazole modified polymer which is configured to ensure that the catalyst contacts the surface of the electrolyte membrane. As used herein, "triazole modified polymer" means that a polymer composition has a triazole substituted or grafted onto the polymer. The triazole modified polymer may comprise various compositions (e.g., polysiloxane). Polysiloxane is believed to be especially advantageous because it has a flexible structure, which provides various benefits for the catalyst layer, such as oxygen permeability. Examples of suitable triazole modified polysiloxanes include 1,2,3-triazole and 1,2,4-triazole, such as shown below.



1,2,4-triazole-grafted polysiloxane



1,2,3-triazole-grafted polysiloxane

Both 1,2,3-triazole and 1,2,4-triazole promote proton conduction via intermolecular proton transfer between the triazole groups (Grotthuss mechanism), and display adequate electrochemical stability under fuel cell operating conditions. Because triazole conducts protons, the catalyst layer does not need humidification (e.g., the catalyst layer is anhydrous), and is thus effective at temperatures above the boiling point of water.

Useful binders may further comprise TEOS (tetraethyl orthosilicate) or other organosiloxane crosslinkers. Furthermore, the catalyst layer may also utilize PVDF (polyvinyldifluoride) to provide additional binding. In some embodiments, the PVDF may be excluded from the binder, because the other components of the binder (e.g., the triazole modified polymer and the organosiloxane crosslinker) may perform the function of the PVDF (i.e., binding the catalyst layer **24** to the electrolyte membrane **10**) (see e.g., FIG. **5**C). Additionally, the binder may comprise solvents (e.g., organic solvents such as methanol, ethanol, propanol, acetone, or combinations thereof).

A catalyst layer utilizing triazole modified polymers (e.g., triazole grafted polysiloxane) and phosphoric acid demonstrates improved properties over other anhydrous high temperature membrane electrode assemblies (e.g., PBI based anhydrous high temperature membrane electrode assemblies). For example, PBI is a thermoplastic polymer with a rigid backbone and a higher glass transition temperature than triazole. As a result of this rigid backbone, PBI electrode assemblies achieve poor proton transfer. Because of its higher glass transition temperature, PBI electrode assemblies demonstrate poor oxygen permeability. PBI electrode assemblies compensate for the poor proton transfer by providing a high concentration of phosphoric acid (e.g. 3.5 to 7.5 H_3PO_4 per PBI repeating unit). In contrast to PBI electrode assemblies, the triazole utilized in the embodiments discussed herein is a stronger acid with a lower pKa value than benzimidazole of the PBI composition, thus triazole is more effective at proton conduction via intermolecular proton transfer between the triazole groups (Grotthuss mechanism). Benzimidazole has a pKa value of about 5.6, whereas 1,2,3-triazole and 1,2,4-triazole have lower pKa values of about 1.2 and 2.19, respectively. Due to these lower pKa values, triazole is significantly better than imidazole at proton transfer; therefore, the present catalyst layer requires less phosphoric acid to achieve the requisite conductivity (3.0 H3PO4 per triazole). With a lower concentration of phosphoric acid, the triazole modified polymer reduces acid leeching and corrosion inside the membrane electrode assembly. Moreover, unlike PBI electrode assemblies, a triazole modified polysiloxane is a polymer having a flexible triazole arm and a flexible polysiloxane backbone. Because triazole modified polysiloxanes are not thermoplastic polymers, they have a lower glass transition temperature than PBI. Due to the flexible backbone as well as a lower glass transition temperature, the triazole modified polysiloxane provides improved oxygen permeability, which also benefits the functionality of the catalyst layer.

A catalyst layer utilizing triazole modified polymers (e.g., triazole grafted polysiloxane) and phosphoric acid demonstrates improved properties over other anhydrous high temperature membrane electrode assemblies (e.g., PBI based anhydrous high temperature membrane electrode assemblies). For example, PBI is a thermoplastic polymer with a rigid backbone and a higher glass transition temperature than triazole. As a result of this rigid backbone, PBI electrode assemblies achieve poor proton transfer. Because of its higher glass transition temperature, PBI electrode assemblies demonstrate poor oxygen permeability. PBI electrode assemblies compensate for the poor proton transfer by providing a high concentration of phosphoric acid (e.g. 3.5 to 7.5 H_3PO_4 moles per PBI repeating unit). In contrast to PBI electrode assemblies, the triazole utilized in the embodiments discussed herein is a stronger acid with a lower pKa value than benzimidazole of the PBI composition, thus triazole is more effective at proton conduction via intermolecular proton transfer between the triazole groups (Grotthuss mechanism). Benzimidazole has a pKa value of about 5.6, whereas 1,2,3-triazole and 1,2,4-triazole have lower pKa values of about 1.2 and 2.19, respectively. Due to these lower pKa values, triazole is significantly better than imidazole at proton transfer; therefore, the present catalyst layer requires less phosphoric acid to achieve the requisite conductivity (3.0 H_3PO_4 moles per moles of triazole). With a lower concentration of phosphoric acid, the triazole modified polymer reduces acid leeching and corrosion inside the membrane electrode assembly. Moreover, unlike PBI electrode assemblies, a triazole modified polysiloxane is a polymer having a flexible triazole arm and a flexible polysiloxane backbone. Because triazole modified polysiloxanes are not thermoplastic polymers, they have a lower glass transition temperature than PBI. Due to the flexible backbone as well as a lower glass transition temperature, the triazole modified polysiloxane provides improved oxygen permeability, which also benefits the functionality of the catalyst layer.

Referring again to the membrane electrode assembly **1** of FIG. **1**, the gas diffusion layer **22** of the fuel cell electrode **20** can be a microporous layer comprising carbon cloth, carbon paper, and combinations thereof. Like the catalyst layer **24**, the electrolyte membrane **10** may comprise triazole modified polysiloxane, and phosphoric acid in order to provide operability at high temperatures and no humidity. The electrolyte membrane **10** may also comprise ePTFE, organosiloxane crosslinkers such as TEOS, or combinations thereof. Due to the polysiloxane and organosiloxane precursor materials present in the catalyst layer **24** and the electrolyte membrane **10**, the interface between electrode and membrane may be very strongly bonded through the Si—O chemical bonds.

Referring to the embodiment of FIG. **2**, a process for producing the catalyst layer (i.e., in situ polymerization from sols) is provided. As shown, the process may comprise providing a binder solution (e.g., binder polymer sol) comprising a triazole modified polymer dissolved in an organic solvent (e.g., an alcohol solvent). In one embodiment, the binder solution may comprise an organosiloxane crosslinker and triazole grafted polysiloxane in a methanol/alcohol solvent, with or without PVDF in polar organic solvent. Meanwhile, the phosphoric acid may be added into the binder solution as a catalyzing reagent as shown in FIG. **2**, or may be doped into the catalyst layer after the catalyst layer is formed via in-situ polymerization.

In addition, the microstructure and performance of the catalyst layer can be impacted by the ordering of the processing steps. For example, when the catalyst layer is formed before adding phosphoric acid (i.e., phosphoric acid is used as a dopant), the sol-gel reactions (i.e., hydrolysis, condensation, and polycondensation) of organosiloxane crosslinker and triazole modified polymer inside the binder is impeded at least partially because the colloidal particles and condensed silica species can not easily link together. Because the sol-gel reactions are partially impeded, the microstructure of the catalyst layer, as shown in FIG. **7**A, demonstrates a layer-shape, wherein the binder **200** is primarily surrounding the Pt catalyst **110** on the C support **100**. The layer structure is further illustrated in the SEM images of FIGS. **8**A and **8**B.

In contrast, when phosphoric acid is added as a catalyzing reagent during catalyst layer formation as shown in FIG. **2**, the phosphoric acid catalyst helps link the colloidal particles and condensed silica species, thereby aiding the hydrolysis, condensation and polycondensation reactions. As a result, the binder **300** is interspersed into the catalysts (e.g., Pt on a C support), thus the microstructure of the catalyst layer defines a cellular-shape microstructure as shown in FIG. **7**B. Because of the addition of catalyzing reagent, the binder is adsorbed onto the catalyst particle surface (e.g., Pt/C). The condensation, polycondensation and gelation reactions are aided by the phosphoric acid catalyzing regent, thus forming cohesion forces between the colloidal organosilicon compound binder and the carbon agglomerates to form a cellular-shape microstructure as shown in FIG. **7**B. This cellular microstructure is further illustrated in the SEM images of FIGS. **9**A and **9**B. The microstructure of FIG. **7**B has an advantage over the microstructure of FIG. **7**A, in that it provides better mass transportation, higher catalyst utilization, and thus higher performance.

From the foregoing, it should be understood that fuel cell electrodes **20** can be formed from the catalyst layers **24** and gas diffusion layers **22**. Formation of fuel cell electrodes **20** may be achieved by the application of the catalyst layer or ink **24** onto a gas diffusion layer **22**. As described above, the catalyst ink **24** comprises at least one catalyst, phosphoric acid, and a binder comprising at least one triazole modified polymer. Further as stated above, the microporous gas diffusion layer **22** comprises carbon paper or carbon cloth. To form fuel cell electrodes **20**, the catalyst ink **24** is applied onto at least one surface of the gas diffusion layer **22** such as shown in FIGS. **3**A and **3**E. The ink may be applied via casting, brushing, spraying, or combinations thereof. When applying the ink, it may be desirable to first heat the gas diffusion layer **22** to a temperature of about 25° C. to about 100° C. by using a heating element such as a hot plate. After the ink is applied, the electrode **20** may be dried (e.g., for several hours at a temperature ranging from about 60° C. to about 130° C.).

Further as shown in FIGS. **3**A-**3**E, the fuel cell electrodes **20** may alternatively be produced by using a mold **30**. In this embodiment, the ink **24** is applied via casting on a thick polytetrafluoroethylene sheet **32** and inside a mold **30** disposed on the polytetrafluoroethylene sheet. The ink **24** may form a layer on the polytetrafluoroethylene sheet as shown in FIG. **3**B. After casting onto the sheet, it may be desirable to evaporate a portion of solvent in the ink **24**. Referring to FIGS. **3**C and **3**D, the gas diffusion layer **22** can be laid on the top surface of the ink **24**, and subsequently dried in air for a period of up to 12 to 24 hours. After drying, the polytetrafluoroethylene sheet **32** and the mold **30** can be removed to produce the electrode **20** as shown in FIG. **3**E.

Upon formation of the electrodes **20**, formation of the membrane electrode assembly **1** includes binding the electrode **20** to the electrolyte membrane **10**. In the embodiment of FIG. **4**A, an electrolyte primer layer **10**A having the same composition as the electrolyte membrane **10** may be coated on a surface of fuel cell electrode **20**, then the electrolyte layer **10**A can be hot-pressed to the electrolyte membrane **10**. Alternatively as shown in FIG. **4**B, the membrane electrode assembly **1** may be formed without the addition of the interposed electrolyte layer **10**A shown in FIG. **4**A. As shown in FIG. **4**B, the catalyst layer **24** can be directly hot pressed to the electrolyte membrane **10**. Although various processing conditions are suitable, the fuel cell electrode **20** may, in one exemplary embodiment, be hot pressed onto the electrolyte membrane **10** at a temperature of about 200° C.

Referring to an alternative embodiment illustrated in FIG. **4**C, the catalyst layer **24** may be coated on both sides of an electrolyte membrane **10**, without the prior step of bonding the catalyst layer **24** to a gas diffusion layer **22** to form an electrode **20**. The coating may occur through spraying, transfer printing, or casting. Referring to FIGS. **5**A through **5**C, a casting process may utilize a mold **30** applied onto the electrolyte membrane **20**. The catalyst layer **24** may be applied as an ink **24** inside the mold **30** onto one or more surfaces of the electrolyte membrane **10**. After the ink forms a layer as shown in FIG. **5**B, the mold **30** is removed as shown in FIG. **5**C.

The aforementioned embodiments of the present invention may be additionally illustrated in view of the Examples provided below:

Example 1

Preparation of Fuel Cell Electrodes

0.01 g of 1,2,4-triazole-grafted polysiloxane, and TEOS and Si-C8 crosslinker (1:1 weight ratio) were dissolved in 5 ml methanol/ethanol (1:1 weight ratio). The binder loading in the electrode was maintained at about 0.125 mg/cm^2. Meanwhile, a 5% PVDF in NMP solvent solution was also produced. Then 0.2 g Pt/C (60% Pt, E-TEK on XC-72 carbon) catalyst was provided at a loading rate of 1-1.5 mg/cm^2, and was then mixed with the above-mentioned PVDF, polysiloxane and crosslinker solutions. Then, the mixed components were stirred for 2 hours, and distributed in the ultrasonic bath for 30 minutes. Thus, the catalyst ink was prepared. 5 g of the catalyst ink was then directly cast on the gas diffusion layer (E-TEK, 100 cm^2). Afterward, the ink was dried carefully in air at room temperature overnight, and then heat-treated at 60° C. for 4 hours, and 130° C. for 30 minutes. After the catalyst layer was formed, the phosphoric acid in water solution was doped on the surface electrode with acid loading of 10 mg/cm^2. The fuel cell electrode was thus prepared.

Example 2

Preparation of Membrane Electrode Assembly

The fuel cell electrode from Example 1 was hot-pressed to a membrane comprising the following components: ePTFE, 1,2,4-triazole-grafted polysiloxane, TEOS and Si-C8 crosslinker) at 200° C., 4 psi for 5 minutes. The MEA was prepared.

Example 3

Comparison with Nafion®-Based Electrodes

Referring to FIG. **6**, the performance of electrodes produced by Example 1 is compared with modified Nafion®-based electrodes. The modified Nafion®-based electrode included Pt loading of 0.5 mg/cm^2, and was modified with a phosphoric acid dopant (acid loading of 20 mg/cm^2 via PA acid in water solution), followed by drying at 110° C. for half an hour. In comparing the fuel cells with Nafion®-based electrode with fuel cells having the electrode of Example 1, the conditions were as follows: The single cell torque was 4N·m. The single fuel cell was operated at 120° C., at ambient pressure of H_2 and O_2 with a flow rate of 10 ml/minute. Referring to FIG. **6**, fuel cells comprising the triazole modified electrodes demonstrate improved properties over fuel cells comprising Nafion®-based electrodes. For instance, fuel cells comprising Nafion®-based electrodes have a peak power density of about 0.10 W/cm^2, whereas the peak power density of the fuel cells comprising triazole based electrodes is at least about 0.22 W/cm^2. In short, fuel cells comprising the electrodes of present invention demonstrate at least a 100% increase in peak power density over fuel cells comprising Nafion®-based electrodes.

Example 4

Preparation of Fuel Cell Electrode with Catalyst Layer Produced Via Phosphoric Acid Dopant

0.01 g 1,2,4-triazole-grafted polysiloxane, and TEOS and Si-C8 crosslinker (1:1 weight ratio) was dissolved in ml methanol/ethanol (1:1 weight ratio). Meanwhile, 0.2 g Pt/C (40% Pt, E-TEK) catalyst with a Pt loading was 1.0 mg/cm^2 was mixed with above-mentioned solution, followed by stirring for 2 hours and distribution in ultrasonic bath for half an hour. Thus, the catalyst ink was prepared. 5 g of the catalyst ink was cast on the gas diffusion layer (E-TEK, 100 cm^2) directly. After the ink was dried carefully in air at room temperature overnight, the ink was heat-treated at 60° C. for 4 hours, and then 130° C. for half an hour in order to form the catalyst layer. After the catalyst layer was formed, the phosphoric acid in water solution was dropped on the surface electrode with acid loading of 20 mg/cm^2. The fuel cell electrode was thus prepared.

Example 5

Preparation of Fuel Cell Electrode with Catalyst Layer Produced Via Phosphoric Acid Catalyzing Reagent

0.01 g 1,2,4-triazole-grafted polysiloxane, and TEOS and Si-C8 crosslinker (1:1 weight ratio) was dissolved in 5 ml methanol/ethanol (1:1, weight ratio). Meanwhile, 0.2 g Pt/C (40% Pt, E-TEK) catalyst with a Pt loading was 1.5 mg/cm^2, 100 mg phosphate acid (equivalent to acid loading of 20 mg/cm^2), were mixed with above-mentioned solution, followed by stirring for 2 hours, and distribution in ultrasonic bath for half an hour. Thus, the catalyst ink was prepared. 5 g of the catalyst ink was cast on the gas diffusion layer (E-TEK, 100 cm^2) directly. After the ink was dried carefully in air at room temperature overnight, the ink was heat-treated at 60° C. for 6 hours, and then 130° C. for 6 hour. The fuel cell electrode was thus prepared.

Example 6

Comparison of Phosphoric Acid Doped Electrodes (Example 4) with Phosphoric Acid Catalyzed Electrodes (Example 5)

To demonstrate the improved properties yielded when phosphoric acid is used as a catalyzing reagent prior to catalyst layer formation, the following experiments were conducted. Each electrode was incorporated into a fuel cell and was evaluated under the following conditions. The single cell torque was 4N·m. The single fuel cell was operated at 120° C. at ambient pressure of H_2 and O_2 with a flow rate of 10 ml/min. Referring to FIG. **10**, the catalyzed phosphoric acid electrode achieved a peak power density of at least about 0.22 W/cm^2, which is significantly higher than the doped phosphoric acid electrode that achieved a peak power density of about 0.05 W/cm^2.

For the purposes of describing and defining the present invention it is noted that the terms "substantially" and "about" are utilized herein to represent the inherent degree of uncertainty that may be attributed to any quantitative comparison, value, measurement, or other representation. These terms are also utilized herein to represent the degree by which a quantitative representation may vary from a stated reference without resulting in a change in the basic function of the subject matter at issue.

Having described the invention in detail and by reference to specific embodiments thereof, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the appended claims. More specifically, although some aspects of the present invention are identified herein as preferred or particularly advantageous, it is contemplated that the present invention is not necessarily limited to these preferred aspects of the invention.

What is claimed is:

1. An anhydrous fuel cell electrode comprising an anhydrous catalyst layer and a gas diffusion layer, wherein the anhydrous catalyst layer comprises:

at least one catalyst,

about 5 mg/cm^2 to about 100 mg/cm^2 of phosphoric acid added as a sol-gel reaction catalyzing reagent during formation of the catalyst layer, and

a binder comprising at least one triazole modified polymer, wherein the triazole modified polymer comprises a polysiloxane backbone and a triazole substituent.

2. The anhydrous fuel cell electrode of claim **1** wherein the catalyst comprises platinum, platinum alloys, carbon, or combinations thereof.

3. The anhydrous fuel cell electrode of claim **1** wherein the triazole modified polymer is selected from the group consisting of 1,2,3-triazole grafted polysiloxane, 1,2,4-triazole grafted polysiloxane, and mixtures thereof.

4. The anhydrous fuel cell electrode of claim **1** wherein the catalyst comprises a catalyst support and the binder is adsorbed onto the catalyst support.

5. The anhydrous fuel cell electrode of claim **1** wherein the fuel cell electrode achieves a peak power density of at least about 0.22 W/cm^2 at 120° C. and ambient pressure.

6. The anhydrous fuel cell electrode of claim **1** wherein the catalyst comprises platinum on a carbon based support.

7. The anhydrous fuel cell electrode of claim **1** wherein the phosphoric acid and the triazole modified polymer define a molar ratio of 3 moles of phosphoric acid per mole of triazole modified polymer.

8. The anhydrous fuel cell electrode of claim **1**, wherein the formed anhydrous catalyst layer defines a cellular microstructure.

9. An anhydrous fuel cell electrode comprising an anhydrous catalyst layer and a gas diffusion layer, wherein the anhydrous catalyst layer comprises:

at least one catalyst comprising platinum,

about 5 mg/cm^2 to about 100 mg/cm^2 of phosphoric acid added as a sol-gel reaction catalyzing reagent during formation of the anhydrous catalyst layer, and

a binder comprising at least one triazole modified polymer, wherein the triazole modified polymer comprises a polysiloxane backbone and a triazole substituent.

10. The anhydrous fuel cell electrode of claim **9** wherein the triazole modified polymer is selected from the group consisting of 1,2,3-triazole grafted polysiloxane, 1,2,4-triazole grafted polysiloxane, and mixtures thereof.

11. The anhydrous fuel cell electrode of claim **9** wherein the platinum catalyst is disposed on a carbon based support.

12. A proton electrolyte membrane fuel cell comprising an electrolyte membrane, and a pair of fuel cell electrodes according to claim **10**, wherein the proton electrolyte membrane fuel cell is operable at temperatures of 120° C.

13. The anhydrous fuel cell electrode of claim **9** wherein the fuel cell electrode achieves a peak power density of at least about 0.22 W/cm^2 at 120° C. and ambient pressure.

14. The anhydrous fuel cell electrode of claim **9**, wherein the formed anhydrous catalyst layer defines a cellular microstructure.

15. A proton electrolyte membrane fuel cell comprising an electrolyte membrane, and a pair of fuel cell electrodes comprising an anhydrous catalyst layer and a gas diffusion layer, wherein the anhydrous catalyst layer comprises:

at least one catalyst,

about 5 mg/cm^2 to about 100 mg/cm^2 of phosphoric acid added as a sol-gel reaction catalyzing reagent during formation of the catalyst layer, and

a binder comprising at least one triazole modified polymer, wherein the triazole modified polymer comprises a polysiloxane backbone and a triazole substituent.

16. The proton electrolyte membrane fuel cell of claim **15** wherein the triazole modified polymer is selected from the group consisting of 1,2,3-triazole grafted polysiloxane, 1,2,4-triazole grafted polysiloxane, and mixtures thereof.

17. The proton electrolyte membrane fuel cell of claim **15** wherein the catalyst is a platinum catalyst is disposed on a carbon based support.

18. The proton electrolyte membrane fuel cell of claim **15** wherein the fuel cell electrode achieves a peak power density of at least about 0.22 W/cm^2 at 120° C. and ambient pressure.

19. The proton electrolyte membrane fuel cell of claim **15** wherein the formed catalyst layer defines a cellular microstructure.

20. The proton electrolyte membrane fuel cell of claim **15** wherein the phosphoric acid and the triazole modified polymer define a molar ratio of 3 moles of phosphoric acid per mole of triazole modified polymer.

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