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(54) **Title**: A MEMBRANE ELECTRODE ASSEMBLY FOR FUEL CELLS

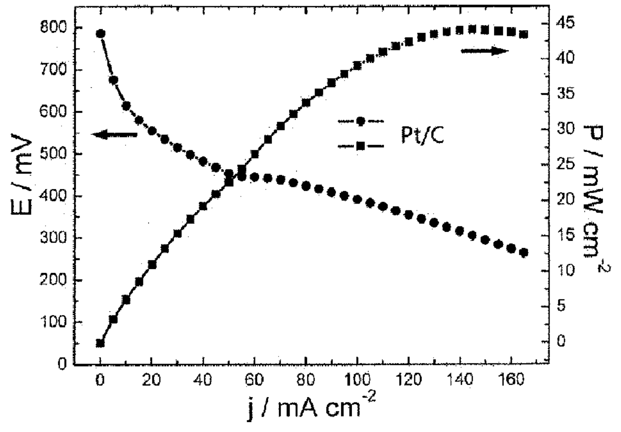

FIG. 1

(57) **Abstract**: A membrane electrode assembly (MEA) for a fuel cell comprising: an anode catalyst which includes a nanoporous gold having one or more coatings of one or more additional metals on its surface where the additional metals are selected from the group comprising: a group (10) element, preferably platinum, a group (15) element, preferably bismuth, or a combination thereof; the anode catalyst is secured to a first side of a proton exchange membrane having a first side and a second side and a cathode catalyst secured to the second side of the proton exchange membrane.

A MEMBRANE ELECTRODE ASSEMBLY FOR FUEL CELLS

Field of the Invention

The invention relates to the field of electrochemical technology, and more specifically relates to a catalyst with low precious metal loading for a fuel cell.

Background of the Invention

Liquid fuel cells, especially direct formic acid fuel cells (DFAFC) and direct methanol fuel cells (DMFC), can effectively convert the chemical energy of liquid fuels into electricity. They have great potential application prospect in portable electronic devices and are expected to become the next generation power source due to their low operating temperature, compact structure, easily portable fuel. Compared with DMFC, DFAFC posses more advantage such as higher open circuit potential and less fuel crossover.

At present, the high price of the catalyst is one of the key issues to inhibit the wide application of direct formic acid fuel cells. The large amount of precious metals used as a catalyst is the primary cause of the fuel cell's high price. In a direct formic acid fuel cell, formic acid is oxidized to protons (H^+), electrons, CO and CO_2 at the anode on a catalyst layer. The protons cross through the proton exchange membrane to the cathode and the electrons are passed through an external circuit to the cathode. The protons and electrons react with oxygen on the cathode catalyst to produce water.

Palladium and platinum are the major catalyst components at the direct formic acid fuel cell anode. Palladium catalysts display higher catalytic activity and the ability of anti-poisoning more readily than platinum. However, palladium's poor stability in an acidic environment severely limits its application. A platinum catalyst is easily poisoned because the carbon monoxide intermediate which is generated seriously hinders the formic acid's direct oxidation pathway.

In order to reduce the cost of the catalyst, the amount of platinum required for a catalyst must be reduced. In order to achieve this goal, traditional method is to prepare the platinum catalyst as a nanoparticle. Amorphous conductive carbon may also be used in the platinum nanoparticle catalysts as a means of support. Though the method of preparing the platinum catalyst as nanoparticles improves the utilization of platinum and thus reduces its cost, there is still a need to improve: 1) platinum utilization; 2) stability (as the catalyst and support connect only by physical adsorption); 3) electron transport (in the conventional ink-process, Nafion should be added for proton transport which leads to decrease of electron transport).

Hence, a need clearly exists for an improved membrane electrode assembly for a fuel cell and a method for making the same.

Summary of the Invention

A membrane electrode assembly (MEA) for a fuel cell comprising: an anode catalyst which includes a nanoporous gold having one or more coatings of one or more additional metals on its surface where the additional metals are selected from the group comprising: a group 10 element, preferably platinum, a group 15 element, preferably bismuth, or a combination thereof; the anode catalyst is secured to a first side of a proton exchange membrane having a first side and a second side and a cathode catalyst secured to the second side of the proton exchange membrane.

Brief Description of the Drawings

FIG.1 illustrates the current-voltage curve and the current-power polarization curve of a commercial Pt/C catalyst.

FIG.2 illustrates the current-voltage curve and the current-power polarization curve of two separate catalysts.

FIG.3 illustrates the current-voltage curve and the current-power polarization curve of two separate catalysts.

FIG.4 illustrates the full cyclic voltammetry(CV) curves of two separate samples.

FIG.5 illustrates the current-voltage curve and the current-power polarization curve of two separate samples.

FIG.6 illustrates the current-voltage curve and the current-power polarization curve of two separate samples.

FIG.7 illustrates the current-voltage curve and the current-power polarization curve of two separate samples.

FIG.8 illustrates the current-voltage curve and the current-power polarization curve of two separate samples.

FIG.9 illustrates the current-voltage curve and the current-power polarization curve of two separate samples.

FIG.10 illustrates the full cyclic voltammetry (CV) curves of a sample.

FIG.11 illustrates the voltage-time curves of two separate samples.

Detailed Description

The present invention relates to a membrane electrode assembly for a fuel cell and a method of making the membrane electrode assembly for a fuel cell. More specifically, the present invention discloses a membrane electrode assembly which includes a catalyst with low precious metal loading for use within a direct formic acid fuel cell. The present invention also discloses a method for creating the membrane electrode assembly.

In order to improve the catalytic activity of a platinum catalyst, one solution is to alloy platinum with some other metal atoms like palladium or ruthenium, or to adsorption deposit some other metal atoms like bismuth or lead onto the surface of platinum.

The chemical or electrochemical corrosion method can be used to prepare the nanoporous metal from an alloy of appropriate composition and proportion in order to provide it with large surface area and a controllable, uniform structure. The nanostructure materials can be used as catalysts, and especially as the electrocatalyst support, because of superior properties such as three dimensional nanostructure, continuous pore structure and pore wall, good electrical conductivity, high surface area, and strong poisoning resistance. The inventors have developed a method of preparing the nanoporous gold supported platinum with surface alloy catalyst by surface modification onto the nanoporous gold supported platinum catalyst. This method can not only improve the platinum utilization greatly and decrease the usage of precious metal, but improve the poisoning resistance performance. Compared to the carbon supported platinum catalyst, the nanoporous gold supported platinum surface alloy catalyst has the following advantages: 1) the nanoporous metal has a three dimensional, double continuous nanoporous structure which favors the conduction of electrons and the diffusion of reactants; 2) platinum is deposited onto the surface of nanoporous gold in the form of atomic layers which has low platinum loading and high utilization; 3) the platinum is combined with the nanoporous gold by metallic bond which has strong structural stability; 4) by other metal atoms modification onto the nanoporous surface, the formed surface alloy improve the poisoning resistance performance.

A. DEFINITIONS

The term “membrane electrode assembly” (MEA), as used herein, refers to the heart of a fuel cell. MEAs contain the electron collectors, the catalyst, and the proton exchange medium. Put another way, an MEA, in its most basic form, is a proton exchange membrane (PEM) sandwiched between two electrodes. The electrodes are the anode and the cathode which are electrically insulated from one another by the PEM. The anode facilitates electrochemical oxidation of the fuel while the cathode promotes the electrochemical reduction of the oxidant. In one embodiment, an MEA may be comprised of an anode, an anode catalyst, a PEM, a cathode and a cathode catalyst. In one embodiment, an MEA may be comprised of an anode diffused layer, an anode catalyst, a PEM, a cathode diffused layer and a cathode catalyst.

The term “proton exchange membrane” (PEM), as used herein, refers to a semipermeable membrane which is permeable to protons, but impermeable to electrons and gases such as oxygen and hydrogen. The PEM is an electrolyte within an MEA and a fuel cell. The semipermeable nature is a PEM’s essential function as part of an MEA within a fuel cell where it acts to separate reactants and transport protons. PEMs may be either pure polymer membranes, composite membranes, or any other type of membrane known in the art. A PEM material may include a sulfonated tetrafluoroethylene based fluoropolymer-copolymer sold by the DuPont Corporation (Wilmington, DE) under the trade name Nafion®.

The term “fuel cell”, as used herein, refers to an electrochemical device that converts the chemical energy of a fuel, along with an oxidant, into electrical energy. A fuel cell is different from a battery in that a fuel cell can continuously supply energy so long as fuel is supplied to the cell. The fuel and the oxidant, usually oxygen, are supplied continuously to a fuel cell from an external source. In contrast, in a battery, the fuel and oxidant are contained within and when the reactants have been consumed, the battery must either be replaced or recharged. One or more membrane electrode assemblies (MEAs) are contained within a fuel cell. Two chemical reactions occur at the interfaces of the three different segments (anode, cathode and electrolyte). The net result of the two reactions is that fuel is consumed, water or carbon dioxide is created, and an electric current is created, which can be used to power electrical devices. At the anode a catalyst oxidizes the fuel which turns the fuel into a positively charged ion, a negatively charged electron, and carbon dioxide. The PEM or electrolyte is a substance specifically designed so ions can pass through it, but the electrons cannot. The freed electrons travel through a wire creating the electric current. The ions travel through the electrolyte to the cathode. Once reaching the cathode, the ions are reunited with the electrons and the two react with a third chemical, usually oxygen, to create water. To deliver the desired amount of energy, fuel cells can be combined in series and/or parallel circuits. Series circuits yield higher voltage while parallel circuits allow a higher current to be supplied. These designs are called a fuel cell stack. The cell surface area can be increased, to allow stronger current from each cell. There are many types of fuel cell known today. In one embodiment of the present invention the fuel cell is a proton exchange membrane fuel cell. In another embodiment of the present invention, the fuel cell is a direct formic acid fuel cell.

The term "catalyst", as used herein, is a substance which modifies and/or increases the rate of a reaction without being consumed in the process. At present, it is necessary to greatly reduce the amount of group 10 elements and group 11 elements which are incorporated into a catalyst in order for fuel cells to achieve economic viability. The instant inventors have discovered that the incorporation of a modified nanoporous gold (NPG) into an MEA within a fuel cell greatly enhances the efficiency of the fuel cell and the electrical output of the fuel cell. In one embodiment of the present invention, a catalyst may refer to an anode catalyst. In another embodiment of the present invention, a catalyst may refer to a cathode catalyst or cathodic catalyst.

The term “NPG”, as used herein, refers to nanoporous gold, which are prepared according the present invention. In one embodiment, NPG refers to a nanoporous gold. In another embodiment, NPG refers to a plurality of particles containing nanostructure gold.

The term “NPG-1Pt”, as used herein, refers to an NPG with one deposition cycle of platinum deposited onto its surface by electrochemical linear scanning from the open circuit potential to the negative potential. In one embodiment of the present invention, platinum is deposited onto a NPG or catalyst from the open circuit potential to 0.3V (versus standard hydrogen electrode) by 50mV/s one time according to the present invention resulting in an NPG-1Pt or catalyst.

The term “NPG-1Pt-Bi”, as used herein, refers to an NPG-1Pt catalyst with a layer of bismuth deposited onto its surface by under potential deposition. In one embodiment of the present invention, bismuth is deposited onto the surface of an NPG-1Pt catalyst at 0.2V (versus standard hydrogen electrode) for 400 seconds according to the present invention resulting in an NPG-1Pt-Bi catalyst.

The term “NPG-10Pt”, as used herein, refers to an NPG with ten deposition cycles of platinum deposited onto its surface by electrochemical linear scanning from the open circuit potential to the negative potential, which is repeated 10 times according to the process of the present invention. In one embodiment of the present invention, a one deposition cycle of platinum is deposited onto the surface of an NPG catalyst from the open circuit potential to 0.3V (versus standard hydrogen electrode) by 50mV/s one time, and then this process is repeating 9 times according to the present invention resulting in an NPG-10Pt catalyst.

The term "NPG-10Pt-Bi", as used herein, refers to an NPG-10Pt catalyst with a layer of bismuth deposited onto its surface by under potential deposition. In one embodiment of the present invention, bismuth is deposited onto the surface of an NPG-10Pt catalyst at 0.2V (versus standard hydrogen electrode) for 400 seconds according to the present invention resulting in an NPG-10Pt-Bi catalyst.

The term "NPG-Pt64", as used herein, refers to a NPG onto which platinum has been deposited for 64 minutes through the use of the hydrazine vapor reduction method according to the present invention.

The term "NPG-Pt64-Bi", as used herein, refers to an NPG-Pt64 catalyst with a layer of bismuth deposited onto its surface by under potential deposition. In one embodiment of the present invention, bismuth is deposited onto the surface of an NPG-Pt64 catalyst at 0.3V (versus standard hydrogen electrode) for 400 seconds according to the present invention resulting in an NPG-Pt64-Bi catalyst.

The term "NPG-Pt8", as used herein, refers to a NPG onto which platinum has been deposited for 8 minutes through the use of the hydrazine vapor method according to the present invention.

The term “NPG-Pt8-Bi”, as used herein, refers to an NPG-Pt8 catalyst with a layer of bismuth deposited onto its surface by under potential deposition. In one embodiment of the present invention, bismuth is deposited onto the surface of an NPG-Pt8 catalyst at 0.2V (versus standard hydrogen electrode) for 400 seconds according to the present invention resulting in an NPG-Pt8-Bi catalyst.

The term “NPG-Pt16”, as used herein, refers to a NPG onto which platinum has been deposited for 16 minutes through the use of the hydrazine vapor method according to the present invention.

The term “NPG-Pt16-Bi”, as used herein, refers to an NPG-Pt16 catalyst with a layer of bismuth deposited onto its surface by under potential deposition. In one embodiment of the present invention, bismuth is deposited onto the surface of an NPG-Pt16 catalyst at 0.2V (versus standard hydrogen electrode) for 400 seconds according to the present invention resulting in an NPG-Pt16-Bi catalyst.

The term “3*NPG-Pt64”, as used herein, refers to a trinal NPG-Pt64 which results when an NPG-Pt64 catalyst is crushed and dispersed in an ethanol solution containing a sulfonated tetrafluoroethylene based fluoropolymer-copolymer (i.e., Nafion®) according to the present invention.

The term “3*NPG-Pt64-Bi”, as used herein, refers to a 3*NPG-Pt64 catalyst with a layer of bismuth deposited onto its surface by under potential deposition. In one embodiment of the present invention, bismuth is deposited onto the surface of an 3*NPG-Pt64 catalyst at 0.2V (versus standard hydrogen electrode) for 400 seconds according to the present invention resulting in a 3*NPG-Pt64-Bi catalyst.

The term “Group 10 elements”, as used herein, includes nickel, palladium and platinum. The term “Group 11 elements”, as used herein, includes copper, silver and gold. The term “Group 15 elements”, as used herein, includes nitrogen, phosphorus, arsenic, antimony and bismuth.

The term “organic dispersion solution”, as used herein, refers to a solution comprising ethanol, isopropyl alcohol, acetone or combinations thereof.

In the present inventions, a 0.05 -50 atomic layer platinum has thickness of 0.01-500nm. Additionally, different atomic layers of platinum have corresponding platinum loading. In one embodiment of the present invention, a 0.05 -50 atomic layer platinum has thickness of 0.25-10nm, because platinum has a certain atomic radius, a 0.05 atomic layer of platinum still has a thickness of the atomic radius. In another embodiment of the present invention, the loading does not reach one atomic layer, that is to say, platinum does not cover with the NPG completely. In still another embodiment of the present invention, a 0.05 -20 atomic layer platinum has thickness of 0.25-4nm. In yet another embodiment of the present invention, a 0.05 -5 atomic layer platinum has thickness of 0.25-1nm.

The term “a coverage of 0.01-0.99”, as used herein, refers to a surface coverage of one material (e.g. NPG or Pt) by another material (e.g. Bi) of between 1% and 99%. In one embodiment, the coverage may be between 0.05 and 0.80. In another embodiment, the coverage may be between 0.1 and 0.65. In still another embodiment, the coverage may be between 0.20 and 0.50. Also in the present invention, a 0.01-0.99 atomic layer bismuth has thickness of about 0.0025-0.5 nm. Additionally, different atomic layers of bismuth have corresponding bismuth loading. In one embodiment of the present invention, a 0.01-0.99 atomic layer bismuth has thickness of about 0.25nm, because bismuth have a certain atomic radius, a 0.05 atomic layer of bismuth still has a thickness of each atomic radius respectively. In another embodiment of the present invention, the loading of bismuth does not reach one atomic layer, that is to say, bismuth dose not cover the NPG-Pt completely. In still another embodiment of the present invention, the 0.01-0,99 atomic layer of bismuth will not reach one atom layer, because if they cover with platinum, the platinum is unable to display it's superior catalytic activity.

B. EMBODIMENTS

The present invention discloses a membrane electrode assembly (MEA) for a fuel cell comprising: an anode catalyst which includes a nanoporous gold having one or more coatings of one or more additional metals selected from the group comprising: a group 10 element, a group 15 element, or a combination thereof on its surface; the anode catalyst is secured to a first side of a proton exchange membrane having a first side and a second side and a cathode catalyst is secured to the second side of the proton exchange membrane. In one embodiment of the present invention, the Group 10 elements include platinum and the Group 15 elements include bismuth. In another embodiment of the present invention, the membrane electrode assembly includes an anode catalyst comprised of a nanoporous gold, one or more layers of platinum bonded to the surface of the nanoporous gold and less than one layer of bismuth bonded to the surface of the platinum. In yet another embodiment of the present invention, the MEA described above may possess the following characteristics: a thickness of 0.05-50μm; a width of 0.1-100cm; a length of 0.2-1000cm; and a three dimensional nanoporous gold structure having an atomic layer of platinum with a uniform thickness of 0.05-50 bonded to its surface and a layer of bismuth atoms having a coverage of 0.01-0.99 bonded to the layer of platinum. In still another embodiment, the membrane electrode assembly as described above may be for use in a direct formic acid fuel cell.

The present invention also discloses a membrane electrode assembly (MEA) for a fuel cell comprising: an anode catalyst which includes a nanoporous gold having one or more coatings of one or more additional metals selected from the group comprising: a group 10 element, a group 11 element, a group 15 element, or a combination thereof on its surface; the anode catalyst is secured to a first side of a proton exchange membrane having a first side and a second side and a cathode catalyst is secured to the second side of the proton exchange membrane. In one embodiment of the present invention, the Group 10 elements include platinum, the Group 11 elements include silver and gold and the Group 15 elements include bismuth. In another embodiment of the present invention, the membrane electrode assembly includes an anode catalyst comprised of a nanoporous gold, one or more layers of platinum bonded to the surface of the nanoporous gold and less than one layer of bismuth bonded to the surface of the platinum. In yet another embodiment of the present invention, the MEA described above may possess the following characteristics: a thickness of 0.05-50μm; a width of 0.1-100cm; a length of 0.2-1000cm; and a three dimensional nanoporous gold structure having an atomic layer of platinum with a uniform thickness of 0.05-50 bonded to its surface and a layer of bismuth atoms having a coverage of 0.01-0.99 bonded to the layer of platinum. In still another embodiment, the membrane electrode assembly as described above may be for use in a direct formic acid fuel cell.

In yet another embodiment of the present invention, the anode catalyst described above may possess the following characteristics: a thickness of 0.05-50μm; a width of 0.1-100cm; a length of 0.2-1000cm; and a three dimensional nanoporous gold structure having an atomic layer of platinum with a uniform thickness of 0.05-50 bonded to its surface and a layer of 0.01-0.99 atoms bismuth bonded to the layer of platinum.

In one embodiment of the present invention, an MEA may be comprised of an anode catalyst which is an NPG-Pt-Bi catalyst, a proton exchange membrane (PEM) and a cathode catalyst. In another embodiment of the present invention, the gold-silver alloy article may be in the range of 0.2-1000 cm long, 0.1-100 cm wide, 0.05-50 um thick, and 10-60% gold (wt.%). In still another embodiment of the present invention, the gold-silver alloy article has a thickness of 100nm-1µm, a width of 1-10cm, and a length of 2-15cm, and comprising 20-50% gold (wt.%).

In one embodiment of the present invention, a layer of platinum having a thickness of 0.01-500nm may be deposited onto the surface of the NPG. In another embodiment, a layer of platinum having a thickness of 0.25-10nm may be deposited onto the surface of the NPG. In yet another embodiment, the PEM used in the MEA is between 0.2 and 10 cm larger than either the NPG-Pt-Bi catalyst or the anode catalyst. In still another embodiment, the PEM used in the MEA is between 0.5 and 2 cm larger than either the NPG-Pt-Bi catalyst or the anode catalyst.

In one embodiment of the present invention, the anode catalyst may be a catalyst ranging from a NPG-Pt1-Bi to a NPG-Pt1000-Bi. In another embodiment, the anode catalyst may be a catalyst ranging from a NPG-Pt1-Bi to a NPG-Pt500-Bi. In still another embodiment, the anode catalyst may be a catalyst ranging from a NPG-Pt 5-Bi to a NPG-Pt100-Bi. In yet another embodiment, the anode catalyst may be a catalyst ranging from a NPG-Pt10-Bi to a NPG-Pt50-Bi. In another embodiment, the anode catalyst may be a NPG-Pt64-Bi catalyst. In still another embodiment, the anode catalyst may be a NPG-Pt16-Bi catalyst. In yet another embodiment, the anode catalyst may be a NPG-Pt8-Bi catalyst.

In another embodiment of the present invention, the anode catalyst may be a catalyst ranging from a NPG-1Pt-Bi catalyst to a NPG-100 Pt-Bi catalyst. In yet another embodiment, the anode catalyst may be a catalyst ranging from a NPG-3Pt-Bi catalyst to a NPG-8Pt-Bi catalyst. In still another embodiment, the anode catalyst may be a NPG10Pt-Bi catalyst. In yet another embodiment, the anode catalyst may be a NPG-5Pt-Bi catalyst. In still another embodiment, the anode catalyst may be a NPG-1Pt-Bi catalyst.

The present invention also discloses a method of preparing a membrane electrode assembly (MEA) comprising the steps of: immersing or placing a gold-silver alloy article in a concentrated nitric acid solution to selectively remove silver from the gold-silver alloy article in order to form a nanoporous gold (NPG); rinsing the NPG in deionized water followed by depositing one or more layers of platinum onto the surface of the NPG wherein the layers of platinum ranging in thickness from sub-monoatomic to a plurality of monoatomic or atomic layers in order to form an NPG-Pt article; and depositing bismuth onto the surface of the NPG-Pt article resulting in an NPG-Pt-Bi catalyst followed by forming the MEA by either:

(1) securing the NPG-Pt-Bi catalyst to a first side of a proton exchange membrane (PEM) having a first side and a second side; securing a cathodic catalyst to the second side of the PEM; and pressing the NPG-Pt-Bi catalyst, the PEM and the cathodic catalyst together to form the MEA; or

(2) dispersing the NPG-Pt-Bi catalyst in ethanol; crushing the NPG-Pt-Bi catalyst; mixing the NPG-Pt-Bi catalyst with a sulfonated tetrafluoroethylene based fluoropolymer-copolymer solution resulting in a coated NPG-Pt-Bi catalyst; brushing or spraying the coated NPG-Pt-Bi catalyst onto a diffused layer to form an anode catalyst; securing the anode catalyst to a first side of a proton exchange membrane (PEM) having a first side and a second side; securing a cathodic catalyst to the second side of the PEM; and pressing the anode catalyst with diffused layer, the PEM and the cathodic catalyst

with diffused layer together to form the MEA.

The present invention includes the preparation methods of making various nanoporous gold supported platinum catalysts by de-alloying gold and silver alloys to obtain a nanoporous gold, which is then modified by methods which include: (i) surface ion adsorption and electrochemical reduction, (ii) under potential deposition (UPD) combined with in-situ replacement, (iii) using a chloroplatinic ion and hydrazine vapor reduction method to deposit the platinum onto the surface of the nanoporous gold, or a combination thereof. The nanoporous gold supported platinum catalyst is then immersed in a perchloric acid solution containing bismuth oxide to form the Bi-modified nonporous gold catalyst supported platinum catalyst.

In order to form the nanoporous gold or nanoporous gold, a gold-silver alloy article is used. In one embodiment of the present invention, the method described above includes a gold-silver alloy article which is 0.2-1000 cm long, 0.1-100 cm wide, 0.05-50 um thick, and 10-60% gold (wt.%). In another embodiment of the present invention, the gold-silver alloy article may have a thickness of 100nm-1µm, a width of 1-10cm, and a length of 2-15cm, and comprising 50% gold (wt.%).

In order to selectively remove silver from a gold-silver alloy article, a concentrated nitric acid solution is used. In one embodiment of the present invention, the method described above includes a gold-silver alloy article being immersed in concentrated nitric acid for a time period ranging from 0.1 to 1000 minutes at a temperature in the range of 0 to 60°C. In another embodiment of the present invention, the method described above includes a gold-silver alloy article being immersed in concentrated nitric acid for a time period ranging from 15 to 60 minutes at a temperature in the range of 20-40°C.

In still another embodiment of the method described above, a layer of platinum may be deposited onto the NPG using a method selected from the group comprising: (1) a surface ion adsorption and electrochemical reduction method; (2) an under potential deposition method combined with in-situ replacement; (3) a chloroplatinic ion solution and hydrazine vapor method; or (4) a combination thereof. Each of these processes results in an NPG-Pt article. In one embodiment of the above method, for option (1) the surface ion adsorption and electrochemical reduction method may be utilized for different thicknesses of NPG wherein a layer of platinum is deposited ranging in thickness from sub-monoatomic to a plurality of atomic layers, and for large platinum loading, the NPG can be adsorbed in a chloroplatinic ion or chloroplatinous ion solution; or for option (2) the under potential deposition method combined with in-situ replacement may be utilized to deposit a layer of platinum having a thickness of 50-500nm onto the surface of NPG; or for option (3) the chloroplatinic ion and hydrazine vapor method may be utilized to deposit a layer of platinum having a thickness of less than 100nm onto the surface of NPG. In still another embodiment of the above method, the concentration of chloroplatinic ion or chloroplatinous ion in option (1) is preferably 0.001-10000mM, the NPG is placed into the chloroplatinic ion or chloroplatinous ion solution for a soaking time period in the range of 1 second to 10 hours and a cleaning step to rinse the chloroplatinic ion or chloroplatinous ion solution from the NPG is completed between 1and 10 times. In another embodiment of the above method, the chloroplatinic ion solution in option (3) has a concentration in the range of 0.1 – 10g/L, has an pH value of between 8-11 and the NPG is exposed to the hydrazine vapor for a period of time ranging from 1-1000 minutes. In yet another embodiment of the above method, the concentration of chloroplatinic ion or chloroplatinous ion in option (1) is preferably 0.5-10mM, the NPG is placed into the chloroplatinic ion or chloroplatinous ion solution for a soaking time period in the range of 3-30 minutes and a cleaning step to rinse the chloroplatinic ion or chloroplatinous ion solution from the NPG is completed between 3 and 6 times. In still another embodiment of the above method, the concentration of the chloroplatinic ion solution in option (3) is 1g/L, the pH value of the chloroplatinic ion solution is 10, and the period of time the NPG is exposed to the hydrazine vapor is in the range of 5-60 minutes.

The method described above includes the process of depositing bismuth onto the surface of a NPG-Pt article. This deposition may be accomplished by any methods known in the art. In one embodiment of the present invention, bismuth is deposited onto the surface of a NPG-Pt article by placing the NPG-Pt article into a perchloric acid solution containing bismuth and adding a 0-0.5V potential (versus standard hydrogen electrode) to the NPG-Pt article for a deposition time period of 1-1000 minutes to obtain an NPG-Pt-Bi catalyst. In another embodiment of the present invention, bismuth is deposited onto the surface of a NPG-Pt article by placing the NPG-Pt article into a perchloric acid solution containing bismuth and soaking the NPG-Pt article for a soaking time period of 1-1000 minutes to obtain an NPG-Pt-Bi catalyst. In still another embodiment of the above method, the concentration of the perchloric acid solution containing Bi is 3-5mM, the deposition potential is 0.2-0.4V (versus standard hydrogen electrode), and the deposition time period is 5-10 minutes or the soaking time period is 5-10 minutes.

Looking at the two methods for forming the MEA described in the method above, in one embodiment of the present invention the sulfonated tetrafluoroethylene based fluoropolymer-copolymer solution has a wt.% of 1-70%. In another embodiment of the present invention, the sulfonated tetrafluoroethylene based fluoropolymer-copolymer solution has a wt.% of 20-40%. In another embodiment of the present invention, the PEM is 0.2 to 10 cm larger than either the cathodic catalyst or the anode catalyst. In still another embodiment of the present invention, the PEM is 0.2 to 10 cm larger than either the NPG-Pt-Bi catalyst or the anode catalyst.

In yet another embodiment of the above described method, the NPG-Pt-Bi catalyst, the PEM and the cathodic catalyst are hot pressed together to form the MEA using a pressure of 0.1-1 MPa cm^{-2} at 20-150°C for 10-1000 seconds. In still another embodiment of the above described method, the anode catalyst, the PEM and the cathodic catalyst are hot pressed together to form the MEA using a pressure of 0.1-1 MPa cm^{-2} at 20-150°C for 10-1000 seconds. In yet another embodiment of above method, the PEM is 0.5 to 2 cm larger than either the NPG-Pt-Bi catalyst or the anode catalyst and the NPG-Pt-Bi catalyst. In still another embodiment, the PEM and the cathodic catalyst are hot pressed together to form the MEA using a pressure of 0.2-0.6 MPa cm^{-2} at 50-140°C for 60-600 seconds; or the anode catalyst, the PEM and the cathodic catalyst are hot pressed together to form the MEA using a pressure of 0.2-0.6 MPa cm^{-2} at 50-140°C for 60-600 seconds.

The present invention can control the catalyst support's surface area by adjusting the thickness and pore size of the nanoporous gold. The present invention can control a catalyst's catalytic activity by adjusting the platinum loading by methods which include: i) regulating the time of adsorption deposition, ii) regulating the time of UPD combined with in-situ replacement, or iii) regulating the time of reduction in hydrazine vapor. The present invention can also control a catalyst's catalytic activity by controlling the amount of platinum deposited onto the NPG and by adjusting the bismuth loading by regulating the deposition potential and deposition time period (or soaking time period). It also can control the fuel cell capability by adjusting the combination of structures in the MEA which are regulated by the hot-press pressure, the hot-press temperature and the hot-press time.

In one embodiment of the present invention, the membrane electrode assembly (MEA) with low precious metal loading for direct formic acid fuel cell prepared by the methods of the present invention may possess the following characteristics: at least one side of the MEA contains a Bi-modified nanoporous gold supported platinum catalyst, and the Bi-modified nanoporous gold supported platinum catalyst has thickness of about 0.05-50μm, width of 0.1-100cm, length of 0.2-1000cm, morphology of three-dimensional nanoporous gold structure which is covered with a uniform thickness of 0.05-50 atomic layer of platinum covered with a layer of bismuth atoms bonded to the nanoporous gold and/or layer of platinum; said layer of bismuth or ruthenium having a coverage of 0.01-0.99 (i.e. covering between 1% and 99% of the platinum).

Compared to the MEA prepared by traditional nanoparticles catalyst supported by carbon, the MEA with low precious metal loading for direct formic acid fuel cell prepared by the method described in the present invention has the following advantages:

(1) NPG has superior electron transfer ability and superior chemical and electrochemical corrosion resistance than the traditional fuel cell catalyst support (like carbon).

(2) The controllable platinum deposition method can control the deposition of platinum in atomic scale, improve the utilization of platinum, and reduce the precious platinum loading by orders of magnitude.

(3) The surface modification can make the adsorption deposited platinum catalyst with good catalytic activity originally improve further, and can make the catalyst with bad catalytic activity originally improve greatly.

(4) The Bi-modified nanoporous gold supported platinum catalyst can not only be brushed (or sprayed, painted) onto the diffusion layer after crushing which it is compatible with the traditional technology, but also it can be directly attached to the proton exchange membrane(PEM) which make the preparing method more simple.

(5) The Bi-modified nanoporous gold supported platinum catalyst prepared by the rational design can decrease the precious metal loading about an order of magnitude.

And it can improve the fuel cell apparent power nearly two times under the condition of decreasing the platinum loading about two orders of magnitude.

C. EXAMPLES

Example 1

1) A 12K gold-silver alloy sample (1.2 cm long, 1 cm wide, 500 nm thick) was placed in concentrated nitric acid for 120 minutes to selectively dissolve silver from the alloy and to form a nanoporous gold (NPG) which was then rinsed and cleaned in deionized water.

2) The NPG was then placed in a mixed solution of 0.1M $HClO_4$ and 1mM H_2PtCl_6 where it soaked for 5 minutes accompanied by electrochemical linear scanning from the open circuit potential to negative potential ended at 0.3V (versus standard hydrogen electrode) by 50mV/s in a three-electrode system in order to form an NPG-1Pt catalyst;

3) The NPG-1Pt catalyst was placed in 0.1M $HClO_4$ solution containing 3mM bismuth in order to deposit bismuth onto the surface of the NPG-1Pt catalyst by adding 0.2V potential (versus standard hydrogen electrode) for 400 seconds to form an NPG-1Pt-Bi catalyst with a diffusion layer of 1*1 cm^2;

4) The NPG-1Pt-Bi catalyst with a diffusion layer of 1*1cm^2 was placed on one side of a proton exchange membrane (PEM) which was 3cm long and 2.8cm wide. A cathodic catalyst was then placed on the other side of the PEM and all three components were then hot-pressed under a pressure of 0.5MPa for 195 seconds at 70°C to form a membrane electrode assembly (MEA). The catalytic activity curves of the NPG-1Pt-Bi catalyst within a direct formic acid fuel cell were shown in FIG.2.

FIG.1 illustrates the current-voltage curve and the current-power polarization curve of a commercial Pt/C catalyst with 2.2mg/cm^2 of platinum loading both in the anode and in the cathode which was operated at 40°C in a direct formic acid fuel cell. 3M HCOOH was pumped into the fuel cell at the anode, and air was pumped in at the cathode as an oxidant. The apparent area of the cell is 1cm^2. The curves show the commercial Pt/C discharge of 44mW at 40°C.

FIG.2 illustrates the current-voltage curve and the current-power polarization curve of a sample having a commercial Pt/C catalyst with 2.2mg/cm^2 platinum loading as a cathode and an NPG-1Pt-Bi catalyst (made by 1 time platinum adsorption-deposition and bismuth under potential deposition) with 0.5mg/cm^2 gold + 0.0025mg/cm^2 platinum loading as an anode and operated at 40°C within a direct formic acid fuel cell. A Membrane Electrode Assembly was hot-pressed at 70°C and 0.5 MPa for 195 seconds. 3M HCOOH was pumped into the fuel cell at the anode, and air was pumped in at the cathode as an oxidant. The apparent area of the cell is 1cm^2. The curves show that the NPG-1Pt-Bi catalyst has a discharge of 39mW at 40°C which is similar capacity as the commercial Pt/C catalyst with 2.2mg/cm^2 platinum loading. FIG. 2 shows that the NPG-1Pt-Bi discharge capacity is 780 times that of the Pt/C catalyst's discharge capacity. Surprisingly, even when each catalyst is normalized to the precious metal mass specific power densities, the NPG-1Pt-Bi catalyst's discharge capacity is 3.9 times that of the Pt/C catalyst.

Example 2

1) A 12K gold-silver alloy sample (1.2 cm long, 1 cm wide, 500 nm thick) was placed in concentrated nitric acid for 120 minutes to selectively dissolve silver from the alloy and to form a nanoporous gold (NPG) which was then rinsed and cleaned in deionized water;

2) The NPG was then placed in the mixed solution of 0.1M $HClO_4$ and 1mM H_2PtCl_6 where it soaked for 5 minutes accompanied by electrochemical linear scanning from the open circuit potential to negative potential ended at 0.3V (versus standard

hydrogen electrode) by 50mV/s in a three electrode system. This process step is repeated 10 times in order to form an NPG-10Pt catalyst;

3) The NPG-10Pt catalyst was placed in 0.1M $HClO_4$ solution containing 3mM bismuth in order to deposit bismuth onto the surface of the NPG-10Pt catalyst by adding 0.2V potential (versus standard hydrogen electrode) for 400 seconds to form a NPG-10Pt-Bi catalyst with a diffusion layer of 1*1cm^2;

4) The NPG-10Pt-Bi catalyst with a diffusion layer of 1*1cm^2 was placed on one side of a proton exchange membrane PEM which was 3cm long and 2.5cm wide). A cathodic catalyst was then placed on the other side of the PEM and all three components were then hot-pressed under a pressure of 0.5MPa for 195 seconds at 70°C to form a membrane electrode assembly (MEA). The catalytic activity curves of an NPG-10Pt-Bi catalyst used within a direct formic acid fuel cell were shown in FIG.3, and the full cyclic voltammery curves were shown in FIG.4.

FIG.3 illustrates the current-voltage curve and the current-power polarization curve of a sample having a commercial Pt/C catalyst with 2.2mg/cm^2 platinum loading as a cathode and an NPG-10Pt-Bi catalyst (made by 10 times platinum adsorption-deposition and bismuth under potential deposition) with 0.5mg/cm^2 gold + 0.025mg/cm^2 platinum loading as an anode, operated at 40°C within a direct formic fuel cell. A Membrane Electrode Assembly was hot-pressed at 70°C and 0.5Mpa for 195 seconds. 3M HCOOH was pumped into the fuel cell at the anode, and air was pumped in at the cathode as oxidant. The apparent area of the cell is 1cm^2. The curves show that the NPG-10Pt-Bi catalyst has a discharge 71mW. This discharge capacity is 1.6 times the discharge capacity of the commercial Pt/C catalyst with 2.2mg/cm^2 platinum loading. Surprisingly, even when each catalyst is normalized to the platinum mass specific power densities, the NPG-10Pt-Bi catalyst's discharge capacity is 142 times that of the Pt/C catalyst. Even more surprisingly, when normalized to the precious metal mass specific power densities, the NPG-10Pt-Bi catalyst's discharge capacity is 6.8 times that of the Pt/C catalyst.

FIG.4 illustrates the full cyclic voltammery(CV) curves of a sample having a commercial Pt/C catalyst with 2.2mg/cm^2 platinum loading as a cathode and an NPG-10Pt-Bi catalyst (made by 10 times platinum adsorption-deposition and bismuth under potential deposition) with 0.5mg/cm^2 gold + 0.025mg/cm^2 platinum loading as an anode in 0.1M $HClO_4$. The curves show the bismuth oxidation peak is at 0.9V.

Example 3

1) A 12K gold-silver alloy sample (1.2 cm long, 1 cm wide, 100 nm thick) was placed in concentrated nitric acid for 15 minutes to selectively dissolve silver from the alloy and to form a nanoporous gold (NPG) which was then rinsed and cleaned in deionized water.

2) The NPG was placed in a 1g/L H_2PtCl_6 solution (pH value is 10), in order to deposit platinum onto the surface of the NPG in N_2H_4 vapor for 64 minutes to form an NPG-Pt64 catalyst.

3) The NPG-Pt64 catalyst was placed in 0.1M $HClO_4$ solution containing 3mM bismuth in order to deposit bismuth onto the surface of the NPG-Pt64 catalyst by adding 0.3V potential (versus standard hydrogen electrode) for 400 seconds to form an NPG-Pt64-Bi catalyst with a diffusion layer of 1*1cm^2.

4) The NPG-Pt64-Bi catalyst with a diffusion layer of 1*1cm^2 was placed on one side of a proton exchange membrane PEM which was 3cm long and 2.8cm wide. A cathodic catalyst was then placed on the other side of the PEM and all three components were then hot-pressed under a pressure of 0.5MPa for 195s at 110°C to form a membrane electrode assembly (MEA). The catalytic activity curves of the direct formic acid fuel cell were shown in FIG.6.

FIG.5 illustrates the current-voltage curve and the current-power polarization curve of a sample having a commercial Pt/C catalyst with 2.2mg/cm^2 platinum loading as a cathode and an NPG-Pt64 catalyst (0.1mg/cm^2 gold + 0.03mg/cm^2 platinum loading) as an anode , operated at 40°C within a direct formic acid fuel cell. A Membrane Electrode Assembly was hot-pressed at 110°C and 0.5Mpa for 195 seconds. 3M HCOOH was pumped into the fuel cell at the anode, and air was pumped in at the cathode as an oxidant. The apparent area of the cell is 1cm^2. The curves show the NPG-Pt64 catalyst discharges 17mW which decreases a lot although it had lower platinum loading compared to the Pt/C catalyst.

FIG.6 illustrates the current-voltage curve and the current-power polarization curve of a sample having a commercial Pt/C catalyst with 2.2mg/cm^2 platinum loading as a cathode and an NPG-Pt64-Bi catalyst (0.1mg/cm^2 gold + 0.03mg/cm^2 platinum loading) as an anode, operated at 40°C within a direct formic acid fuel cell. A Membrane Electrode Assembly was hot-pressed at 110°C and 0.5Mpa for 195 seconds. 3M HCOOH was pumped into the fuel cell at the anode, and air was pumped in at the cathode as an oxidant. The apparent area of the cell is 1cm^2. The curves show that the NPG-Pt64-Bi catalyst discharged 33mW, which demonstrates a higher discharge capacity than the NPG-Pt64 catalyst with the same platinum loading. Though the capacity is lower than commercial Pt/C, normalized to the platinum mass specific power densities, the NPG-Pt64-Bi discharge capacity is 55 times that of Pt/C. Surprisingly, even when each catalyst is normalized to the precious metal mass specific power densities, the NPG-Pt64-Bi catalyst's discharge capacity is 12.7 times that of the Pt/C catalyst.

Example 4

1) A 12K gold-silver alloy sample (1.5 cm long, 1 cm wide, 100 nm thick) was placed in concentrated nitric acid for 15 minutes to selectively dissolve silver from the

alloy to form a nanoporous gold (NPG) which is then rinsed and cleaned in deionized water.

2) The NPG was placed in 1g/L H_2PtCl_6 solution (pH value is 10) in order to deposit platinum onto the surface of the NPG in N_2H_4 vapor for 8 minutes resulting in an NPG-Pt8 catalyst.

3) The NPG-Pt8 catalyst was then placed in a solution of 0.1M $HClO_4$ containing 5mM bismuth in order to deposit bismuth onto the surface of the NPG-Pt8 catalyst by adding 0.2V potential (versus standard hydrogen electrode) for 400 seconds to form an NPG-Pt8-Bi catalyst with a diffusion layer of 1*1cm^2.

4) The NPG-Pt8-Bi catalyst with a diffusion layer of 1*1cm^2 was placed on one side of a proton exchange membrane PEM which was 3cm long and 2.7cm wide. A cathodic catalyst was then placed on the other side of the PEM and all three components were then hot-pressed under a pressure of 0.5MPa for 195 seconds at 110°C to form a membrane electrode assembly (MEA). The catalytic activity curves of the direct formic acid fuel cell were shown in FIG.7.

FIG.7 illustrates the current-voltage curve and the current-power polarization curve of a sample having a commercial Pt/C catalyst with 2.2mg/cm^2 platinum loading as a cathode and an NPG-Pt8-Bi catalyst (0.1mg/cm^2 gold + 0.006mg/cm^2 platinum loading) as an anode, operated at 40°C within a direct formic acid fuel cell. The NPG-Pt8-Bi catalyst was prepared by de-alloying a 12K Ag-Au alloy with 68%(wt.%) and a thickness of 100nm in nitric acid for 15 minutes at 30°C to create an NPG, followed by depositing platinum onto the surface of the NPG for 8 minutes to create an NPG-Pt catalyst, followed by modifying bismuth onto the NPG-Pt catalyst at 0.2V (versus standard hydrogen electrode) for 400 seconds resulting in an NPG-Pt8-Bi catalyst. A membrane electrode assembly was hot-pressed at 110°Cand 0.5Mpa for 195 seconds. 3M HCOOH was pumped into the fuel cell at the anode, and air was pumped in at the cathode as an oxidant. The apparent area of the cell is 1cm^2. The curves show that the NPG-Pt8-Bi catalyst discharged 60mW which demonstrates a higher discharge capacity (1.4 times) than of the Pt/C with 2.2mg/cm^2 platinum loading. Normalized to the platinum mass specific power densities, the NPG-Pt8-Bi catalyst's discharge capacity is 500 times that of the Pt/C catalyst. Surprisingly, even when each catalyst is normalized to the precious metal mass specific power densities, the NPG-Pt8-Bi catalyst's discharge capacity is 28 times that of the Pt/C catalyst.

Example 5

1) A 12K gold-silver alloy sample (1.5 cm long, 1 cm wide and100 nm thick) was placed in concentrated nitric acid for 15 minutes to form a nanoporous gold NPG which is then cleaned and rinsed in deionized water;

2) The NPG was then placed in a 1g/L H_2PtCl_6 solution (pH value is 10), in order to deposit platinum onto the surface of the NPG in N_2H_4 vapor for 16 minutes to form an NPG-Pt16 catalyst;

3) The NPG-Pt16 catalyst was then placed in solution of 0.1M $HClO_4$ containing 5mM bismuth in order to deposit bismuth onto the surface of the NPG-Pt16 catalyst by adding 0.2V potential (versus standard hydrogen electrode) for 400 seconds to form an NPG-Pt16-Bi catalyst with a diffusion layer of 1*1cm^2;

4) The NPG-Pt16-Bi catalyst with a diffusion layer of 1*1cm^2 was placed on one side of a proton exchange membrane (PEM) which was 3cm long and 2.8cm wide. A cathodic catalyst was then placed on the other side of the PEM and all three components were then hot-pressed under a pressure of 0.5MPa for 195 seconds at 110°C to form a membrane electrode assembly (MEA). The catalytic activity curves of the direct formic acid fuel cell were shown in FIG.8.

FIG.8 illustrates the current-voltage curve and the current-power polarization curve of a sample having a commercial Pt/C catalyst with 2.2mg/cm^2 platinum loading as a cathode and an NPG-Pt16-Bi catalyst (0.1mg/cm^2 gold + 0.01mg/cm^2 platinum loading) as an anode, operated at 40°C within a direct formic acid fuel cell. The NPG-Pt16-Bi catalyst was prepared by de-alloying a 12K Ag-Au alloy with 68%(wt.%) nitric acid and a thickness of 100nm in nitric acid for 15 minutes at 30°C to create an NPG, followed by depositing platinum onto the surface of the NPG for 16 minutes to create an NPG-Pt catalyst, followed by modifying bismuth onto the NPG-Pt16 catalyst at 0.2V (versus standard hydrogen electrode) 400seconds resulting in an NPG-Pt16-Bi catalyst. A membrane electrode assembly was hot-pressed at 110°Cand 0.5Mpa for 195 seconds. 3M HCOOH was pumped into the fuel cell at the anode, and air was pumped in at the cathode as an oxidant. The apparent area of the cell is 1cm^2. The curves show that the NPG-Pt16-Bi catalyst discharged 80mW which demonstrates a higher discharge capacity (1.8 times) than that of the Pt/C catalyst with 2.2mg/cm^2 platinum loading. Normalized to the platinum mass specific power densities, the NPG-Pt16-Bi catalyst's discharge capacity is 400 times that of the Pt/C catalyst. Surprisingly, even when each catalyst is normalized to the precious metal mass specific power densities, the NPG-Pt16-Bi catalyst's discharge capacity is 36 times that of the Pt/C catalyst.

Example 6

1) A 12K gold-silver alloy sample (1 cm long, 1 cm wide, 100 nm thick) was placed in concentrated nitric acid for 15 minutes to form a nanoporous gold (NPG) which is then cleaned and rinsed in deionized water.

2) The NPG was then placed in a 1g/L H_2PtCl_6 solution (pH value is 10), in order to deposit platinum onto the surface of the NPG in N_2H_4 vapor for 64 minutes to form an NPG-Pt64 catalyst.

3) The NPG-Pt64 catalyst was placed in 0.1M solution of $HClO_4$ containing 5mM bismuth in order to deposit bismuth onto the surface of the NPG-Pt64 catalyst by adding

0.2V potential (versus standard hydrogen electrode) for 400 seconds to make NPG-Pt64-Bi catalyst. The NPG-Pt64-Bi catalyst was crushed and dispersed in an ethanol solution followed by the addition of a Nafion® solution and then brushed onto carbon paper to form a 3*NPG-Pt64-Bi catalyst with a diffusion layer of 1*1cm^2.

4) The 3*NPG-Pt64-Bi catalyst with a diffusion layer of 1*1cm^2 was then placed on one side of a proton exchange membrane PEM which was 3 cm long and 2.8 cm wide. A cathodic catalyst was then placed on the other side of the PEM and all three components were then hot-pressed under a pressure of 0.5MPa for 195 seconds at 110°C to form a membrane electrode assembly (MEA). The catalytic activity curves of the direct formic acid fuel cell were shown in FIG.9, the full CV curves were shown in FIG.10 and the stability curve was shown in FIG.11.

FIG.9 illustrates the current-voltage curve and the current-power polarization curve of a sample having a commercial Pt/C catalyst with 2.2mg/cm^2 platinum loading as a cathode and a 3*NPG-Pt64-Bi catalyst (0.3mg/cm^2 gold + 0.09mg/cm^2 platinum loading) as an anode, operated at 40°C within a direct formic acid fuel cell. The 3*NPG-Pt64-Bi catalyst was prepared by crushing and dispersing a NPG-Pt64-Bi catalyst into an ethanol solution with a 30% Nafion® solution and then brushing onto a diffusion layer. A Membrane Electrode Assembly was hot-pressed at 110°C and 0.5Mpa for 195 seconds. 3M HCOOH was pumped into the fuel cell at the anode, and air was pumped in at the cathode as an oxidant. The apparent area of the cell is 1cm^2. The curves show that the 3*NPG-Pt64-Bi catalyst discharged 78mW which demonstrates a higher discharge capacity (1.7 times) than that of the Pt/C catalyst with 2.2mg/cm^2 platinum loading. Normalized to the platinum mass specific power densities, the 3*NPG-Pt64-Bi catalyst's discharge capacity is 43 times that of the Pt/C catalyst. Surprisingly, even when each catalyst is normalized to the precious metal mass specific power densities, the 3*NPG-Pt64-Bi catalyst's discharge capacity is 10 times that of the Pt/C catalyst.

FIG.10 illustrates the full cyclic voltammery (CV) curves of a sample having a commercial Pt/C catalyst with 2.2mg/cm^2 platinum loading as a cathode and a 3*NPG-Pt64-Bi catalyst (0.3mg/cm^2 gold + 0.09mg/cm^2 platinum loading) as an anode in 0.1M $HClO_4$. The curves show a bismuth oxidation peak is at 0.9V.

FIG. 11 illustrates the voltage-time curves at a constant current density of 200mA/cm^2 operated at 40°C within a direct formic acid fuel cell. The sample is a commercial Pt/C catalyst with 2.2mg/cm^2 platinum loading as a cathode and a 3*NPG-Pt64-Bi catalyst with 0.3mg/cm^2 gold + 0.09mg/cm^2 platinum loading as an anode. 3M HCOOH was pumped into the fuel cell at the anode. The 3*NPG-Pt64-Bi catalyst was prepared by brushing the crushed trinal NPG-Pt64-Bi catalyst with a 30% Nafion® solution onto the diffusion layer. A Membrane Electrode Assembly was hot-pressed at 110°C and 0.5Mpa for 195 seconds. 3M HCOOH was pumped into the fuel cell at the anode, and air was pumped in at the cathode as an oxidant. The apparent area of the cell is 1cm^2. The curves show that, at the constant current density of 200mA/cm^2, the cell potential had good stability and remained stable at 330mV after preliminary activation.

WHAT IS CLAIMED IS

1. A membrane electrode assembly (MEA) for a fuel cell comprising:

an anode catalyst which includes a nanoporous gold having one or more coatings of one or more additional metals on its surface;

said additional metals being selected from the group comprising: a group 10 element, a group 15 element, or a combination thereof

said anode catalyst being secured to a first side of a proton exchange membrane having a first side and a second side;

a cathode catalyst secured to said second side of said proton exchange membrane.

2. The membrane electrode assembly of claim 1 wherein said group 10 elements being platinum and having a thickness of less than 500nm and said group 15 elements being bismuth and having a thickness of less than 10nm.

3. The membrane electrode assembly of claim 1 wherein said anode catalyst being comprised of a nanoporous gold, one or more layers of platinum bonded to the surface of said nanoporous gold and one or more layers of bismuth bonded to the surface of said nanoporous gold and/or said platinum.

4. The membrane electrode assembly of claim 1 wherein said anode catalyst having the following characteristics:

a thickness of 0.05-50μm;

a width of 0.1-100cm;

a length of 0.2-1000cm; and

a three dimensional nanoporous gold structure having an atomic layer of deposited platinum with a 0.05-50 atomic layer thickness bonded to its surface and a layer of bismuth atoms bonded to said nanoporous gold and/or said layer of platinum;

said layer of bismuth having a coverage of 0.01-0.99.

5. The membrane electrode assembly of claim 1 wherein said fuel cell being a direct formic acid fuel cell.

6. A method of preparing a membrane electrode assembly (MEA) comprising the steps of:

immersing a gold-silver alloy article in a concentrated nitric acid solution to selectively remove silver from said gold-silver alloy article in order to form a nanoporous gold (NPG);

rinsing said NPG in deionized water;

depositing one or more layers of platinum onto the surface of said NPG wherein said layers of platinum ranging in thickness from sub-monoatomic to a plurality of monoatomic or atomic layers in order to form an NPG-Pt article;

depositing bismuth onto the surface of the NPG-Pt article resulting in an NPG-Pt-Bi catalyst;

forming said MEA by either

(1) securing said NPG-Pt-Bi catalyst to a first side of a proton exchange membrane (PEM) having a first side and a second side;

securing a cathodic catalyst to said second side of said PEM;

pressing said NPG-Pt-Bi catalyst, said PEM and said cathodic catalyst together to form said MEA; or

(2) dispersing said NPG-Pt-Bi catalyst in an organic dispersion solution;

crushing said NPG-Pt-Bi catalyst;

mixing said NPG-Pt-Bi catalyst with a sulfonated tetrafluoroethylene based fluoropolymer-copolymer solution resulting in a coated NPG-Pt-Bi catalyst;

brushing or spraying said coated NPG-Pt-Bi catalyst to form a diffused layer which is an anode catalyst;

securing said anode catalyst to a first side of a proton exchange membrane (PEM) having a first side and a second side;

securing a cathodic catalyst to said second side of said PEM;

pressing said anode catalyst, said PEM and said cathodic catalyst together to form said MEA.

7. The method according to claim 6 wherein said gold-silver alloy article being 0.2-1000 cm long, 0.1-100 cm wide, 0.05-50 um thick, and 10-60% gold (wt.%).

8. The method according to claim 6 wherein said gold-silver alloy article being immersed in concentrated nitric acid for a time period ranging from 0.1 to 1000 minutes at a temperature in the range of 0 to 60°C.

9. The method according to claim 6 wherein said layer of platinum being deposited onto said NPG using a method selected from the group comprising: (1) a surface ion adsorption and electrochemical reduction method; (2) an under potential deposition method combined with in-situ replacement; (3) a chloroplatinic ion and hydrazine vapor method, or a combination thereof.

10. The method according to claim 9 wherein for option (1) the surface ion adsorption and electrochemical reduction method may be utilized for different thicknesses of NPG wherein a layer of platinum is deposited ranging in thickness from sub-monoatomic to a plurality of atomic layers, and for large platinum loading, the NPG can be adsorbed in a chloroplatinic ion or chloroplatinous ion solution, wherein the

concentration of the chloroplatinic ion or chloroplatinous ion solution being 0.001-10000mM, the NPG is placed into the chloroplatinic ion or chloroplatinous ion solution for a soaking time period in the range of 1 second to 10 hours, and a cleaning step to rinse the chloroplatinic ion or chloroplatinous ion solution from the NPG is completed between 1and 10 times; or for option (2) the under potential deposition method combined with in-situ replacement may be utilized to deposit a layer of platinum having a thickness of 50-500nm onto the surface of NPG; or for option (3) the chloroplatinic ion and hydrazine vapor method may be utilized to deposit a layer of platinum having a thickness of less than 100nm onto the surface of NPG and wherein the concentration of the chloroplatinic ion solution being 0.1 – 10g/L, having an pH value of between 8-11 and wherein the NPG is exposed to the hydrazine vapor for a period of time ranging from 1-1000 minutes.

11. The method according to claim 6 wherein bismuth is deposited onto the surface of the NPG-Pt article by:

placing said NPG-Pt article into a perchloric acid solution containing bismuth and adding a 0-0.5V potential (versus standard hydrogen electrode) to said NPG-Pt article for a deposition time period of 1-1000 minutes to obtain an NPG-Pt-Bi catalyst; or

placing said NPG-Pt article into a perchloric acid solution containing bismuth and soaking said NPG-Pt article for a soaking time period of 1-1000 minutes to obtain an NPG-Pt-Bi catalyst.

12. The method according to claim 6 wherein said gold-silver alloy article having a thickness of 100nm-1μm, a width of 1-10cm, and a length of 2-15cm, and comprising 50% gold (wt.%).

13. The method according to claim 8 wherein said gold-silver alloy article being immersed in concentrated nitric acid for a time period ranging from 15 to 60 minutes at a temperature in the range of 20-40°C.

14. The method according to claim 10 wherein the concentration of said chloroplatinic ion solution being 1g/L, the pH value of said chloroplatinic ion solution being 10, and said period of time being in the range of 5-60 minutes.

15. The method according to claim 11, wherein the concentration of said perchloric acid solution containing Bi being 3-5mM, said deposition potential being 0.2-0.4V (versus standard hydrogen electrode), and said deposition time period being 5-10 minutes or said soaking time period being 5-10 minutes.

16. The method according to claim 6, wherein said sulfonated tetrafluoroethylene based fluoropolymer-copolymer solution having a wt.% of 1-70%.

17. The method according to claim 6, wherein said PEM being 0.2 to 10 cm larger than either the NPG-Pt-Bi catalyst or the anode catalyst.

18. The method according to claim 6, wherein the pressing of:

said NPG-Pt-Bi catalyst, said PEM and said cathodic catalyst to form said MEA being hot-pressed under 0.1-1 MPa cm^{-2} at 20-150°C for 10-1000 seconds; or

said anode catalyst, said PEM and said cathodic catalyst to form said MEA being hot-pressed under 0.1-1 MPa cm^{-2} at 20-150°C for 10-1000 seconds.

19. The method according to claim 16 wherein said sulfonated tetrafluoroethylene based fluoropolymer-copolymer solution having a wt.% of 20-40%.

20. The method according to claim 6 wherein said PEM being 0.5 to 2 cm larger than either the NPG-Pt-Bi catalyst or the anode catalyst and wherein the pressing of:

said NPG-Pt-Bi catalyst, said PEM and said cathodic catalyst to form said MEA being hot-pressed under 0.2-0.6 MPa cm^{-2} at 50-140°C for 60-600 seconds; or

said anode catalyst, said PEM and said cathodic catalyst to form said MEA being hot-pressed under 0.2-0.6 MPa cm^{-2} at 50-140°C for 60-600 seconds.

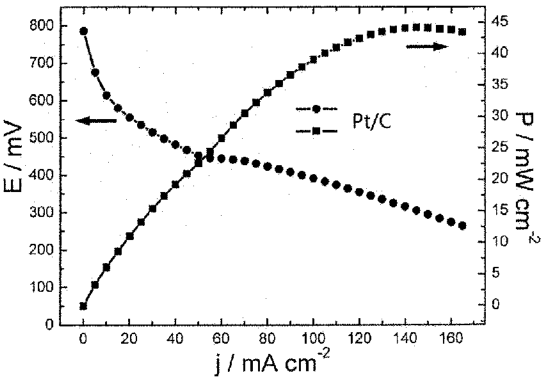

FIG. 1

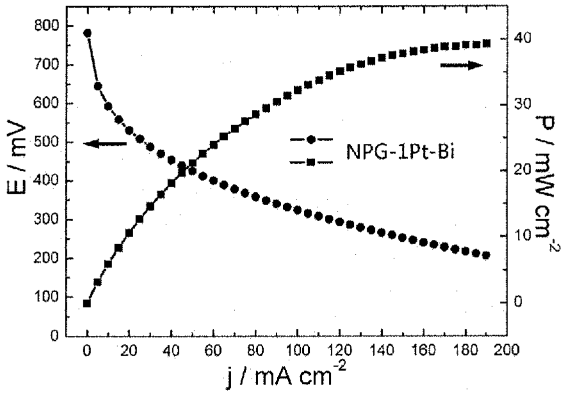

FIG. 2

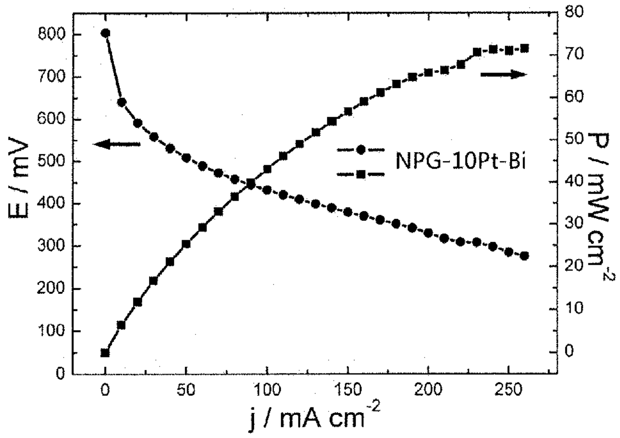

FIG. 3

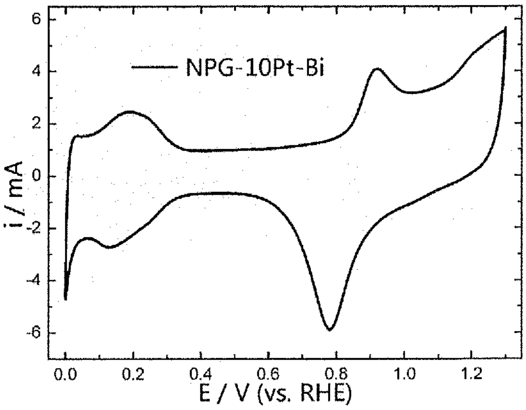

FIG.4

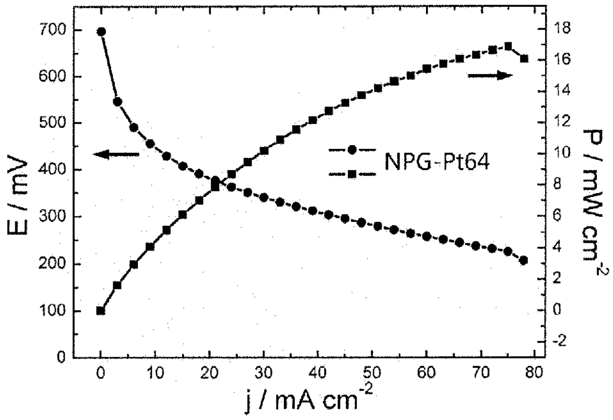

FIG. 5

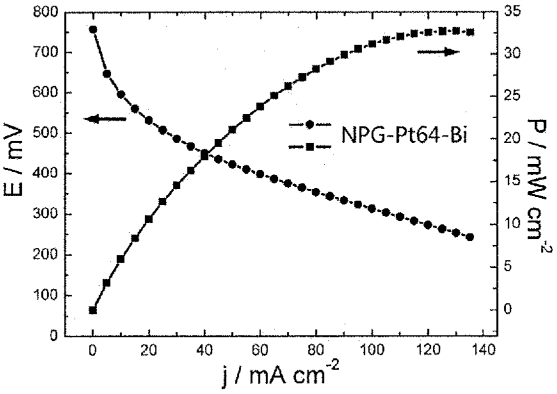

FIG. 6

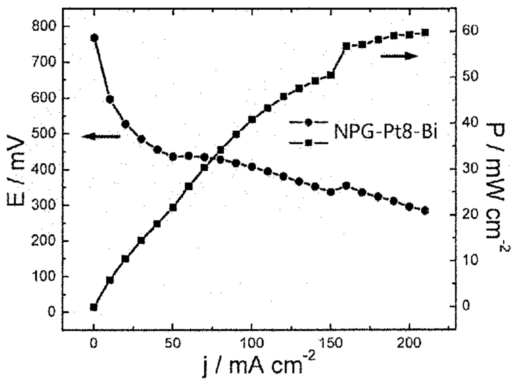

FIG. 7

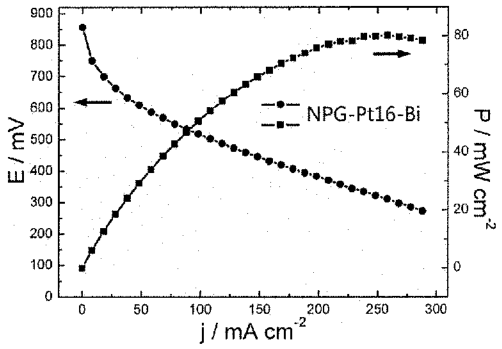

FIG.8

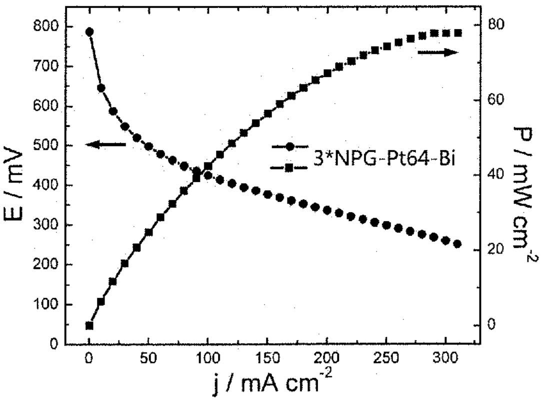

FIG. 9

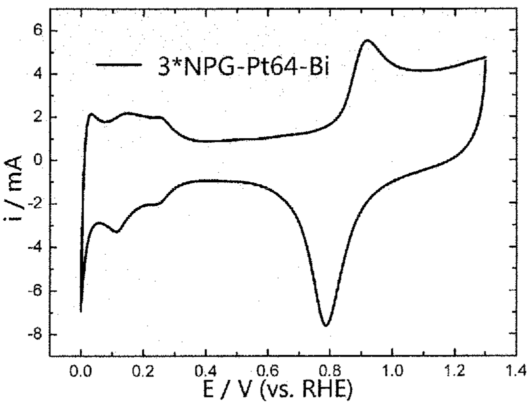
3*NPG-Pt64-Bi
i / mA
6
4
2
0
-2
-4
-6
-8
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
E / V (vs. RHE)

FIG. 10

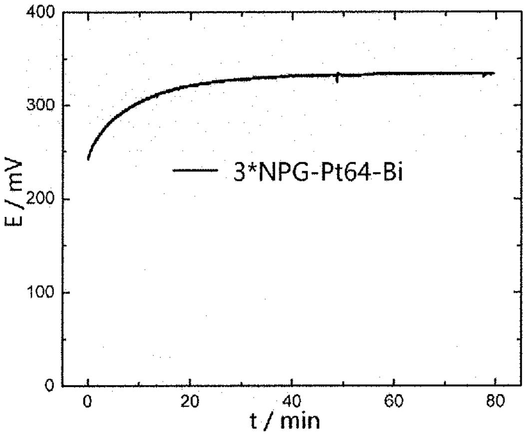
3*NPG-Pt64-Bi
E / mV
400
300
200
100
0
0
20
40
60
80
t / min

FIG.11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2011/022550

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01M 4/90 (2011.01)
USPC - 502/344
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8) - H01M 4/86, 4/88, 4/90, 4/92 (2011.01)
USPC - 429/405, 484, 523, 524; 502/100, 300, 344; 977

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)
Orbit, Google Patents

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2005/0112432 A1 (ERLEBACHER et al) 26 May 2005 (26.05.2005) entire document	1-2 --- 3-20
Y	US 7,632,779 B1 (DING et al) 15 December 2009 (15.12.2009) entire document	3-20
Y	US 2010/0316931 A1 (WIELAND) 16 December 2010 (16.12.2010) entire document	11, 15
Y	US 2004/0229077 A1 (MORI et al) 18 November 2004 (18.11.2004) entire document	1-20

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 15 March 2011	Date of mailing of the international search report 25 MAR 2011
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774