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(71) Applicant (for all designated States except US): **BLUE NANO, INC.** [US/US]; 17325 Connor Quay Court, Cornelius, NC 28031-6502 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **DING, Yi** [CN/CN]; Blue Nano 2-B-213, No. 19 Hua Neng Road, Jinan, Shandong, 250100 (CN). **WANG, Rong, Yue** [CN/CN]; Blue Nano 2-B-213, No. 19 Hua Neng Road, Jinan, Shandong, 250100 (CN).(74) Agents: **VANDE GARDE, Blake, E** et al.; Hammer & Associates, P.C., 3125 Springbank Lane, Suite G, Charlotte, NC 28226 (US).

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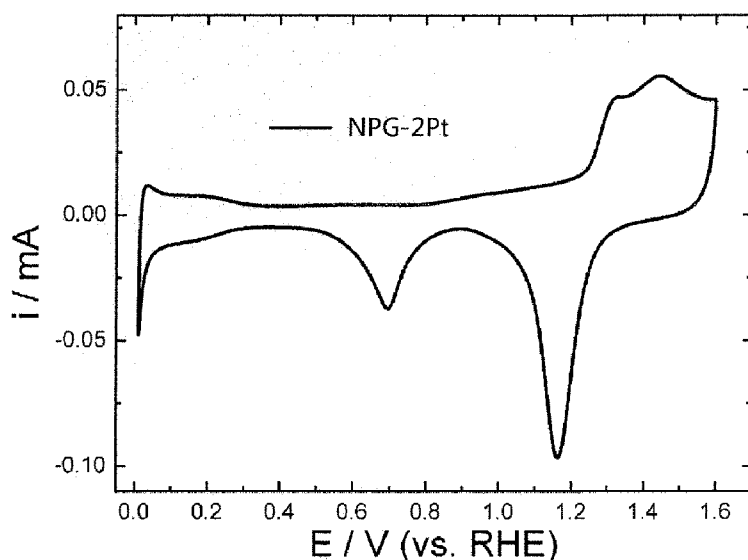


FIG. 1

(57) Abstract: 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 the NPG in deionized water; immersing the NPG in chloroplatinic ion or chloroplatinous ion solution for a soaking time period followed by rinsing and cleaning in deionized water; depositing one or more layers of platinum onto the surface of the NPG in order to form an NPG-Pt catalyst; forming the MEA by securing the NPG-Pt catalyst to a first side of a proton exchange membrane (PEM); securing a cathodic catalyst to the second side of the PEM; and pressing the NPG-Pt catalyst, the PEM and the cathodic catalyst together to form the MEA.

METHOD FOR PREPARING AN MEA FOR A FUEL CELL

Field of the Invention

The invention belongs to the field of electrochemical technology, and relates to a catalyst base on nanoporous gold (NPG) for fuel cell, in particular, relates to the NPG supported ultra-low Pt catalyst for direct formic acid fuel cells anode.

Background of the Invention

A fuel cell is an energy conversion device that converts the chemical energy into electricity through reactions between the fuel and an oxidant. The benefits of fuel cells include a high efficiency of energy conversion and no (or low) pollution.

The fuel cell technology development is particularly urgent in light of the energy crisis and serious environment pollution caused by the over-exploitation of traditional fossil fuel. Proton exchange membrane fuel cells (PEMFCs) with solid proton exchange membrane as electrolyte are ideal for vehicle and other mobile facilities for power because of the low operating temperature and compact structure advantages. The fuel of the PEMFCs includes gaseous hydrogen and liquid small organic molecules, such as methanol, formic acid, ethanol, acetic acid, dimethyl ether and so on. The fuel cell with liquid small organic molecules as fuel is called direct liquid fuel cell, and the direct methanol and direct formic acid fuel cells are particularly widespread researched. The direct liquid fuel cells show significant advantages over hydrogen fuel cells in fuel supply, so the direct liquid fuel cells have great application potential in portable electronic devices such as laptop computers and cell phones, attracting more and more researchers and energy companies' attention.

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 by carbon monoxide intermediate which seriously hinders the formic acid's direct oxidation pathway. Small Pt atomic ensembles let formic acid oxidize in the direct pathway, and large ensembles produce carbon monoxide poisoning easily. In order to reduce the catalyst loading, we should improve the catalytic activity and poisoning resistance capability on one hand, and improve the utilization of Pt on the other hand. Traditional method is to dispersing the Pt nanoparticles onto the conductor carrier like carbon powders, but the Pt utilization is still low (20-30%).

Karl Sieradzki and R. C. Newman reported a method of forming a porous gold structure by the electrochemical etching a gold-silver alloy in 1990. (K. Sieradzki, R. C. Newman "Micro- and Nano-porous Metallic Structures" US Patent, 4,977,038, Dec. 11, 1990). Recently the current inventors have developed a new method of plating a porous metal surface by depositing precious metals with catalytic activity in the form of ultra-low loading onto the surface of a nanoporous metal by surface ion adsorption combined with electrochemical reduction. Studies have indicated that the catalyst with ultra-low precious

metal loading prepared by surface ion adsorption combined with electrochemical reduction displays excellent electro-catalytic properties toward formic acid electrooxidation. The reason for these properties is that in a catalyst prepared by this method, the platinum atoms are highly dispersed on the surface of the nanoporous gold which allows formic acid oxidation to be carried out by a direct pathway and to improve the catalyst's resistance to poisoning.

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 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 the NPG in deionized water; immersing the NPG in chloroplatinic ion or chloroplatinous ion solution for a soaking time period followed by rinsing and cleaning in deionized water; depositing one or more layers of platinum onto the surface of the 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 catalyst; forming the MEA by securing the NPG-Pt 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 catalyst, the PEM and the cathodic catalyst together to form the MEA.

Brief Descriptions of the Drawings

FIG.1 illustrates the full cyclic voltammetry (CV) curves of NPG-2Pt in 0.1M HClO₄.

FIG.2 illustrates the full cyclic voltammetry (CV) curves of NPG-2Pt in a mixed solution of 0.1M HClO₄ and 0.1M HCOOH.

FIG.3 illustrates the current-voltage curve and the current-power polarization curve of a commercial Pt/C catalyst.

FIG.4 illustrates the current-voltage curve and the current-power polarization curve 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 current-voltage curve and the current-power polarization curve of two separate samples.

FIG.11 illustrates the full cyclic voltammetry (CV) curves of MEA with NPG-10Pt catalyst.

Detailed Description

The present invention is to provide a method of preparing a catalyst with ultra-low precious metal loading for fuel cell, in particular, to provide a method of preparing nanoporous gold supported ultra-low platinum catalyst by surface ion adsorption combined with electrochemical reduction method for the direct formic acid fuel cell anode.

The present invention shows the preparation method of making nanoporous gold supported platinum catalyst by depositing platinum onto the surface of NPG through ion adsorption combined with chemical reduction method, controlling the deposition platinum loading and atomic ensembles by adjusting the times of adsorption deposition. The NPG was made from gold and silver alloys. The nanoporous gold supported platinum catalyst with diffusion layer is then placed on one side of a proton exchange membrane (PEM), with a cathodic catalyst on the other side of PEM which is then hot-pressed under a certain pressure at a certain temperature for a certain amount of time to join the diffusion layer, catalysts and PEM into a membrane electrode assembly (MEA). The present invention can control the fuel cell performance by adjusting the thickness and pore size of the nanoporous gold (NPG); adjusting the platinum loading and surface structure by regulating the times of adsorption deposition onto the NPG, adjusting the combination of structures by regulating the hot-press pressure, hot-press temperature and hot-press time.

The membrane electrode assembly (MEA) with low precious metal loading for direct formic acid fuel cell anode prepared by the method in the present invention has these characteristics, the MEA contains a nanoporous gold supported platinum catalyst at least on one side, the nanoporous gold supported platinum catalyst has thickness of about 0.05-50um, 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 0.05-20 atomic layer of platinum.

A. DEFINITIONS

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 "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 “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 “NPG-2Pt”, as used herein, refers to an NPG with two deposition cycles of platinum deposited onto its surface. In one embodiment, platinum is adsorption deposited onto the surface of NPG by electrochemical linear scanning from the open circuit potential to the negative potential (0V, versus standard hydrogen electrode) by 50mV/s, which is repeated 2 times according to the process of the present invention. In another embodiment of the present invention, a one deposition cycle of platinum is deposited onto the surface of an NPG from the open circuit potential to 0.3V (versus standard hydrogen electrode) by 50mV/s one time, and then this process is repeating 1 time according to the present invention resulting in an NPG-2Pt catalyst.

The term “NPG-10Pt”, as used herein, refers to an NPG with ten deposition cycles of platinum deposited onto its surface. In one embodiment, platinum is adsorption deposited onto the surface of NPG by electrochemical linear scanning from the open circuit potential to the negative potential (0V, versus standard hydrogen electrode) by 50mV/s, which is repeated 10 times according to the process of the present invention. In another embodiment of the present invention, a one deposition cycle of platinum is

deposited onto the surface of an NPG 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.

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, 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 another embodiment of the present invention, a 0.05 -20 atomic layer platinum has thickness of 0.25-4nm. In still another embodiment of the present invention, a 0.05 -5 atomic layer platinum has thickness of 0.25-1nm.

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 platinum 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 secured to the second side of the proton exchange membrane. In one embodiment of the present invention, the anode catalyst has the following characteristics: a thickness of 0.05-50 μ m; 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. 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, the platinum which is coated onto said anode catalyst has a thickness of less than 500nm. In still another embodiment of the present invention, the NPG described above may possess the following characteristics: a thickness of 0.05-50 μ m; a width of 0.1-100cm; a length of 0.2-1000cm.

In one embodiment of the present invention, an MEA may be comprised of an anode catalyst which is an NPG-Pt 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 μ m thick, and 10-60% gold (wt.%). In still another embodiment of the present invention, the gold-silver alloy article has a thickness of 100nm-1 μ m, 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 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 catalyst or the anode catalyst.

In another embodiment of the present invention, the anode catalyst may be a catalyst ranging from a NPG-1Pt catalyst to a NPG-100Pt catalyst. In still another embodiment, the anode catalyst may be a catalyst ranging from a NPG-1Pt catalyst to a NPG-50Pt catalyst. In still another embodiment, the anode catalyst may be a catalyst ranging from a NPG-1Pt catalyst to a NPG-10Pt catalyst. In yet another embodiment, the anode catalyst may be a catalyst ranging from a NPG-3Pt catalyst to a NPG-8Pt catalyst.

In still another embodiment, the anode catalyst may be a NPG10Pt catalyst. In yet another embodiment, the anode catalyst may be a NPG-5Pt catalyst. In still another embodiment, the anode catalyst may be a NPG-1Pt catalyst.

The present invention discloses 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 the NPG in deionized water; immersing the NPG in a chloroplatinic ion or chloroplatinous ion solution for a soaking time period followed by rinsing and cleaning in deionized water; depositing one or more layers of platinum onto the surface of the 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 catalyst; forming the MEA by securing the NPG-Pt 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 catalyst, the PEM and the cathodic catalyst together to form the MEA.

In one embodiment of the present invention, the gold-silver alloy article is 0.2-1000 cm long, 0.1-100 cm wide, 0.05-50 μm thick, and 10-60% gold (wt.%). In another embodiment of the above method, the gold-silver alloy article having a thickness of 100nm- 2 μm , a width of 1-10cm, and a length of 2-15cm, and comprising 50% gold (wt.%). In another embodiment of the above method, the gold-silver alloy article is immersed in concentrated nitric acid for a time period ranging from 1 to 1000 minutes at a temperature in the range of 0 to 60°C. In yet another embodiment of the above method, the layer of platinum is deposited onto the NPG using a surface ion adsorption combined with electrochemical reduction method. In still another embodiment of the above method, the surface ion adsorption combined with 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 solution. In yet another embodiment of the above method, the gold-silver alloy article is 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 one embodiment of the above method, one or more layers of platinum are deposited onto the surface of the NPG by: a) placing the NPG into a 0.000001-10M chloroplatinic ion or chloroplatinous ion solution; b) soaking the NPG for a soaking time period of between 1 second and 10 hours; c) cleaning the NPG in deionized water 1-10 times to eliminate chloroplatinic ion solution from the pores of the NPG; d) adding a reduction potential (below 0.6V versus standard hydrogen electrode) to the NPG for 0.01 seconds - 1 hour to deoxidize the chloroplatinic ion or chloroplatinous ion; or e) adding an electrochemical scan from open circuit to 0V to deoxidize the chloroplatinic ion or chloroplatinous ion adsorbed on the NPG; and f) repeating steps a) through e) 0-1000times to deposit additional platinum onto the surface of the NPG. In another embodiment of the above method, the reduction potential described in step d) is 0-0.4V, the reduction time is 1-10 seconds, or adding an electrochemical scan from open circuit potential to 0V. In still another embodiment of the above method, step f) is repeated between 0-100 times. In yet another embodiment of the above method, step f) is repeated between 3-50 times. In still another embodiment of the above method, step f) is repeated between 5-10 times.

In one embodiment of the above method, the PEM is 0.2 to 10 cm larger than the NPG-Pt catalyst or the cathodic catalyst. In another embodiment of the above method, the NPG-Pt catalyst, the PEM and the cathodic catalyst are hot pressed together under a pressure of $0.1\text{--}1\text{ MPa cm}^{-2}$ at a temperature of $20\text{--}150^{\circ}\text{C}$ for a time period of 10-1000 seconds. In yet another embodiment of the above method, the concentration of the chloroplatinic ion or chloroplatinous ion solution is in the range of 0.5-10mM, the soaking time period is 3-30 minutes and the cleaning times is 3-6 times. In still another embodiment of the above method, the PEM is 0.5 to 2 cm larger than either the NPG-Pt catalyst or the cathodic catalyst and wherein the NPG-Pt catalyst, the PEM and the cathodic catalyst are hot-pressed together under a pressure of $0.2\text{--}0.6\text{ MPa cm}^{-2}$ at a temperature of $50\text{--}140^{\circ}\text{C}$ for a time period of 60-600 seconds.

The method disclosed in the present invention fully retains the catalyst's advantages prepared by the ion adsorption combined with electrochemical reduction method, and is compatible with current fuel cell technology as well. When compared to an MEA prepared by a traditional nanoparticles catalyst supported by carbon, an MEA with a nanoporous gold supported platinum catalyst and low precious metal loading for a direct formic acid fuel cell anode prepared by the method described in the present invention has the following advantages: (1) the NPG has superior conductivity than carbon powders; (2) In catalyst prepared by the ion adsorption combined with electrochemical reduction method, the metallic bond combination between platinum and gold is stronger than the physical adsorption between platinum nanoparticles and carbon powder, which improves the catalyst stability; (3) In catalyst prepared by the ion adsorption combined with electrochemical reduction method, the utilization of platinum is higher (almost 100%), and can be used to control the catalyst's activity by adjusting the atomic ensembles.

The sole method used to deposit platinum onto an NPG in the present invention is the adsorption deposition method. The inventors of the present invention found that the alternate methods of depositing platinum onto an NPG (the under potential deposition and the hydrazine vapor methods) result in poor catalytic activity without the addition of further modification.

C. EXAMPLES

Example 1

1) A 9K gold-silver alloy sample (2 cm long, 1 cm wide, 100 nm thick) was placed in concentrated nitric acid for 120 minutes at 20°C 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 1mM H_2PtCl_6 where it soaked for 5 minutes after which it was cleaning in deionized water 6 times to eliminate H_2PtCl_6 in the pores of the NPG.

3) The NPG supported platinum catalyst was then prepared by electrochemical scanning from open circuit potential to 0V (versus standard hydrogen electrode) to deoxidize the chloroplatinic ion adsorbed on the NPG.

4) Processes 2) and 3) are then repeated one time to obtain an NPG-2Pt catalyst. The electrochemical CV curves and electro-catalytic curves of formic acid were shown in FIG.1 and FIG.2.

FIG.1 illustrates the full cyclic voltammetry (CV) curves of an NPG-2Pt catalyst in 0.1M HClO_4 , made by de-alloying a 9 karat (K), 100 nm thick Ag-Au alloy in 68%(wt.%) nitric acid for 120 minutes at 20°C resulting in an NPG, followed by subjecting the NPG to platinum adsorption-deposition 2 times to obtain the NPG-2Pt. The curves show that the platinum oxidation peak is around 0.8-1.2V, the gold oxidation peak is around 1.3-1.6V;

the gold reduction peak is around 0.9-1.4V, the platinum reduction peak is around 0.5-0.9V and the hydrogen under potential adsorption-desorption peaks on the platinum surface are between 0-0.4V. It is clear from these peaks that platinum has been successfully deposited onto the surface of the nanoporous gold and the coverage is about 30%.

FIG.2 illustrates the full cyclic voltammetry (CV) curves of NPG-2Pt catalyst in a mixed solution of 0.1M HClO₄ and 0.1M HCOOH. The current has been normalized to the platinum loading. The HCOOH oxidation starting peak is at 0.2V and the oxidation current is high, which shows the HCOOH oxidize through the direct pathway. The current is normalized to the platinum loading and has been improved by about two orders of magnitude compared to the commercial catalyst which shows that the catalyst has high catalytic activity and good poisoning resistance capability.

FIG.3 illustrates the current-voltage curve and the current-power polarization curve of commercial Pt/C catalyst with 2.2mg/cm² platinum loading both on the anode and the cathode operated at 40°C within a direct formic acid fuel cell. 3M HCOOH was pumped in at the anode, and air was pumped in at the cathode as oxidant. The apparent area of the cell is 1cm². The curve shows commercial Pt/C discharge 44mW at 40°C and the power density is normalized to the platinum loading is 20 mW mg⁻¹.

Example 2

1) A 12K gold-silver alloy sample (1.3 cm long, 1 cm wide, 500 nm thick) was placed in concentrated nitric acid for 120 minutes at 30°C to form a nanoporous gold (NPG) which was then rinsed and cleaned in deionized water.

2) The NPG was then placed in a 1mM H_2PtCl_6 where it soaked for 5 minutes after which it was cleaning in deionized water 3 times to eliminate H_2PtCl_6 in the pores of the NPG.

3) The NPG supported platinum catalyst was then prepared by electrochemical scanning from open circuit potential to 0V (versus standard hydrogen electrode) to deoxidize the chloroplatinic ion adsorbed on the NPG.

4) Processes 2) and 3) are then repeated 9 times to obtain an NPG-10Pt catalyst.

5) The NPG-10Pt catalyst with a diffusion layer of $1 \times 1 \text{ cm}^2$ was placed onto 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 discharge curves and stability curve are shown in FIG.4 and FIG.5.

FIG.4 illustrates the current-voltage curve and the current-power polarization curve of sample having a commercial Pt/C catalyst with 2.2 mg/cm^2 platinum loading as a cathode and an NPG-10Pt catalyst (made by 10 times platinum adsorption-deposition on NPG) as an anode, operated at 40°C within a direct formic acid fuel cell. The NPG was prepared by de-alloying a 12 karat (K), $0.5 \mu\text{m}$ thick Ag-Au alloy in 68%(wt.%) concentrated nitric acid for 120 minutes at 30°C . A membrane electrode assembly (MEA) 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 1 cm^2 . The curves show that the NPG-10Pt catalyst has a maximum power of 45mW at 40°C . Surprisingly, even when maximum power is normalized to the platinum loading, the NPG-10Pt catalyst's power density is 3460 mW mg^{-1} , which means that the catalyst's discharge capacity is 173 times that of the Pt/C catalyst. Even more surprisingly, when normalized to the total anode precious metal, the NPG-10Pt catalyst

discharge capacity is 88 mW mg^{-1} , which means that the catalyst's discharge capacity is 4.4 times that of the Pt/C catalyst.

FIG.5 illustrates the voltage-time curves of an NPG-10Pt catalyst at a constant current density of 50 mA/cm^2 operated at 40°C within a direct formic acid fuel cell. The apparent area of the cell is 1 cm^2 . The curves show that an NPG-10Pt catalyst made from a 12 karat (K), $0.5 \mu\text{m}$ thick Ag-Au alloy which is then hot-pressed at 70°C is stable after around 10 to 20 minutes of activation and it displays good stability.

Example 3

1) A 12K gold-silver alloy sample (1.3 cm long, 1 cm wide, 100 nm thick) was placed in concentrated nitric acid for 30 minutes at 30°C to form a nanoporous gold (NPG) which was then rinsed and cleaned in deionized water.

2) The NPG was placed in $1 \text{ mM H}_2\text{PtCl}_6$ where it soaked for 5 minutes after which it was cleaning in deionized water 6 times to eliminate H_2PtCl_6 in the pores of the NPG.

3) The NPG supported platinum catalyst by was then prepared by electrochemical scanning from open circuit potential to 0V (versus standard hydrogen electrode) to deoxidize the chloroplatinic ion adsorbed on the NPG.

4) Processes 2) and 3) were then repeated 9 times to obtain an NPG-10Pt catalyst.

5) The NPG-10Pt catalyst with a diffusion layer of $1 \times 1 \text{ cm}^2$ was placed onto 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 70°C to form a membrane electrode assembly (MEA). The discharge curves were shown in FIG.6.

FIG.6 illustrates the current-voltage curve and the current-power polarization curve of a sample having a commercial Pt/C catalyst with $2.2\text{mg}/\text{cm}^2$ platinum loading as a cathode and an NPG-10Pt catalyst (made by 10 times platinum adsorption-deposition on NPG) as an anode, operated at 40°C within a direct formic acid fuel cell. The NPG was prepared by de-alloying a 12 karat (K), 100nm thick Ag-Au alloy in 68%(wt.%) concentrated nitric acid for 30 minutes at 30°C . A membrane electrode assembly (MEA) 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 catalyst has a maximum power of 22.5mW at 40°C . Surprisingly, even when the maximum power is normalized to the platinum loading, the NPG-10Pt catalyst's power density is 3210 mW mg^{-1} , which means that the catalyst's discharge capacity is 160 times that of the Pt/C catalyst. Even more surprisingly, when normalized to the total anode precious metal, the NPG-10Pt catalyst discharge capacity is 210 mW mg^{-1} , which means that the catalyst's discharge capacity is 10.5 times that of the Pt/C catalyst.

Example 4

1) A 12K gold-silver alloy sample (1.3 cm long, 1 cm wide, 500 nm thick) was placed in concentrated nitric acid for 120 minutes at 30°C to form a nanoporous gold (NPG) which was then rinsed and cleaned in deionized water.

2) The NPG was placed in 1mM H_2PtCl_6 where it soaked for 5 minutes after which it was cleaning in deionized water 3 times to eliminate H_2PtCl_6 in the pores of the NPG.

3) The NPG supported platinum catalyst was then prepared by electrochemical scanning from open circuit potential to 0V (versus standard hydrogen electrode) to deoxidize the chloroplatinic ion adsorbed on the NPG.

4) Processes 2) and 3) are then repeated 9 times to obtain an NPG-10Pt catalyst.

5) The NPG-10Pt catalyst with a diffusion layer of $1 \times 1 \text{ cm}^2$ was placed onto 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 110°C to form a membrane electrode assembly (MEA). The discharge curves and stability curve were shown in FIG.7, FIG.8, FIG.9 and FIG.10, the electrochemical CV curves was shown in FIG.11.

FIG.7 illustrates the current-voltage curve and the current-power polarization curve of a sample having a commercial Pt/C catalyst with 2.2 mg/cm^2 platinum loading as a cathode and an NPG-10Pt catalyst (made by 10 times platinum adsorption-deposition on NPG) as an anode, operated at 40°C within a direct formic acid fuel cell. The NPG was prepared by de-alloying a 12 karat (K), $0.5 \mu\text{m}$ thick Ag-Au alloy in 68%(wt.%) concentrated nitric acid for 120 minutes at 30°C . A membrane electrode assembly (MEA) 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 oxidant. The apparent area of the cell is 1 cm^2 . The curves show that the NPG-10Pt catalyst has a maximum power of 49mW at 40°C . Surprisingly, even when the maximum power is normalized to the platinum loading, the NPG-10Pt catalyst's power density is 3770 mW mg^{-1} , which means that the catalyst's discharge capacity is 189 times that of the Pt/C catalyst. Even more surprisingly, when normalized to the total anode precious metal, the NPG-10Pt catalyst discharge capacity is 96 mW mg^{-1} , which means that the catalyst's discharge capacity is 4.8 times that of the Pt/C catalyst.

FIG.8 illustrates the current-voltage curve and the current-power polarization curve of a sample having a commercial Pt/C catalyst with 2.2 mg/cm^2 platinum loading as a cathode and an NPG-10Pt catalyst (made by 10 times platinum adsorption-deposition on

NPG) as an anode, operated at 60°C within a direct formic acid fuel cell. The NPG was prepared by de-alloying a 12 karat (K), 0.5µm thick Ag-Au alloy in 68%(wt.%) concentrated nitric acid for 120 minutes at 30°C. A membrane electrode assembly (MEA) 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 oxidant. The apparent area of the cell is 1cm². The curves show that the NPG-10Pt catalyst has a maximum power of 80mW at 60°C. Surprisingly, even when the maximum power is normalized to the platinum loading, the NPG-10Pt catalyst's power density is 6150 mW mg⁻¹.

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/cm² platinum loading as a cathode and an NPG-10Pt catalyst (made by 10 times platinum adsorption-deposition on NPG) as an anode, operated at 80°C within a direct formic acid fuel cell. The NPG was prepared by de-alloying a 12 karat (K), 0.5µm thick Ag-Au alloy in 68% (wt.%) concentrated nitric acid for 120 minutes at 30°C. A membrane electrode assembly (MEA) 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 oxidant. The apparent area of the cell is 1cm². The curves show that the NPG-10Pt catalyst has a maximum power of 102mW at 80°C. Surprisingly, even when the maximum power is normalized to the platinum loading, the NPG-10Pt catalyst's power density is 7850 mW mg⁻¹.

FIG.10 illustrates the voltage-time curves of an NPG-10Pt catalyst at constant current density of 200mA/cm² operated at 80°C within a direct formic acid fuel cell. The apparent area of the cell is 1cm². The curves show that an NPG-10Pt catalyst made from a 12 karat (K), 0.5µm thick Ag-Au alloy which is then hot-pressed at 110°C is stable after around 10 to 20 minutes of activation and it displays good stability.

FIG.11 illustrates the full cyclic voltammetry (CV) curves of an NPG-10Pt catalyst in 0.1M HClO₄, made by de-alloying a 12 karat (K), 0.5µm thick Ag-Au alloy in 68%(wt.%) nitric acid for 120 minutes at 30°C resulting in an NPG, followed by subjecting the NPG to platinum adsorption-deposition 10 times to obtain the NPG-10Pt. A membrane electrode assembly (MEA) was hot-pressed at 110°C and 0.5Mpa for 195 seconds. The curves show that the platinum oxidation peak is around 0.8-1.2V, the gold oxidation peak is around 1.3-1.6V; the gold reduction peak is around 0.9-1.4V, the platinum reduction peak is around 0.5-0.9V, and the hydrogen under potential adsorption-desorption peaks on platinum surface are between 0-0.4V. It is clear from these peaks that platinum has been successfully deposited onto the surface of the nanoporous gold and the coverage is about 60%.

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 platinum on its surface;
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 anode catalyst having the following characteristics:
a thickness of 0.05-50 μ m;
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.
3. The membrane electrode assembly of claim 1 wherein said fuel cell being a direct formic acid fuel cell.
4. The catalyst for a fuel cell of claim 1 wherein said platinum which is coated onto said anode catalyst having a thickness of less than 500nm.
5. 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;

immersing said NPG in a chloroplatinic ion or chloroplatinous ion solution for a soaking time period followed by rinsing and cleaning 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 catalyst;

forming said MEA by securing said NPG-Pt 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 catalyst, said PEM and said cathodic catalyst together to form said MEA.

6. The method according to claim 5 wherein said gold-silver alloy article being 0.2-1000 cm long, 0.1-100 cm wide, 0.05-50 μm thick, and 10-60% gold (wt.%).

7. The method according to claim 5 wherein said gold-silver alloy article being immersed in concentrated nitric acid for a time period ranging from 1 to 1000 minutes at a temperature in the range of 0 to 60°C.

8. The method according to claim 5 wherein said layer of platinum is deposited onto said NPG using a surface ion adsorption combined with electrochemical reduction method;

9. The method according to claim 8 wherein the surface ion adsorption combined with 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 solution.

10. The method according to claim 5 wherein said gold-silver alloy article having a thickness of 100nm- 2 μ m, a width of 1-10cm, and a length of 2-15cm, and comprising 50% gold (wt.%).

11. The method according to claim 7 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.

12. The method according to claim 5 wherein one or more layers of platinum are deposited onto the surface of said NPG by:

a) placing said NPG into 0.000001-10M chloroplatinic ion or chloroplatinous ion solution;

b) soaking said NPG for a soaking time period of between 1 second and 10 hours;

c) cleaning said NPG in deionized water 1-10 times to eliminate chloroplatinic ion solution from the pores of said NPG;

d) adding a reduction potential (below 0.6V versus standard hydrogen electrode) to said NPG for 0.01seconds-1hour to deoxidize the chloroplatinic ion or chloroplatinous ion; or

e) adding an electrochemical scan from open circuit to 0V to deoxidize the chloroplatinic ion or chloroplatinous ion adsorbed on the NPG; and

f) repeating steps a) through e) 0-1000times to deposit additional platinum onto the surface of said NPG.

13. The method according to claim 5 wherein said PEM being 0.2 to 10 cm larger than the NPG-Pt catalyst or the cathodic catalyst.

14. The method according to claim 5 wherein said NPG-Pt catalyst, said PEM and said cathodic catalyst being hot pressed together under a pressure of 0.1-1 MPa cm⁻² at a temperature of 20-150°C for a time period of 10-1000 seconds.

15. The method according to claim 12 wherein the concentration of said chloroplatinic ion or chloroplatinous ion solution being in the range of 0.5-10mM, the soaking time period being 3-30 minutes and the cleaning times being 3-6 times.

16. The method according to claim 12 wherein said reduction potential described in step d) being 0-0.4V, the reduction time being 1-10seconds, or adding an electrochemical scan from open circuit potential to 0V.

17. The method according to claim 12 wherein step f) being repeated between 0-100 times.

18. The method according to claim 5 wherein said PEM being 0.5 to 2 cm larger than either the NPG-Pt catalyst or the cathodic catalyst and wherein said NPG-Pt catalyst, said PEM and said cathodic catalyst being hot-pressed together under a pressure of 0.2-0.6 MPa cm⁻² at a temperature of 50-140°C for a time period of 60-600 seconds.

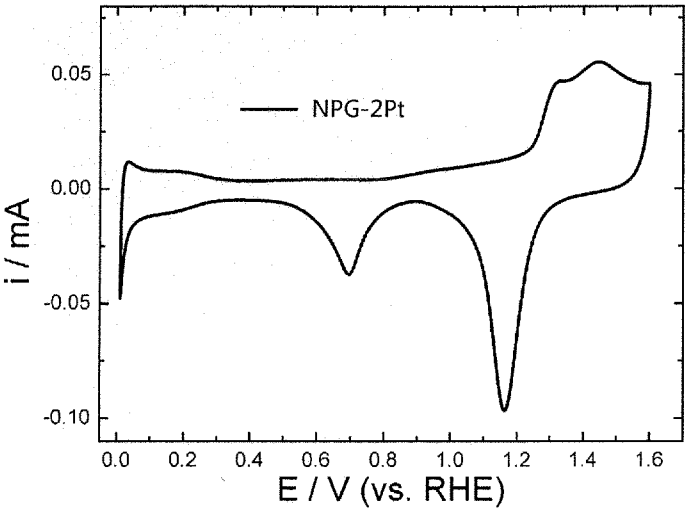


FIG. 1

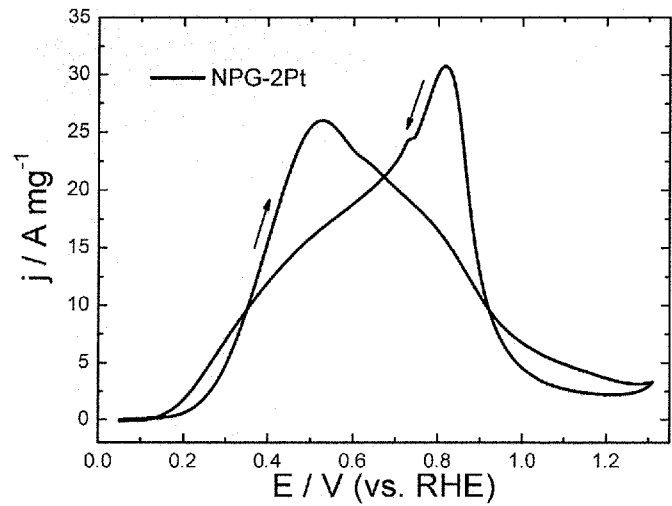


FIG. 2

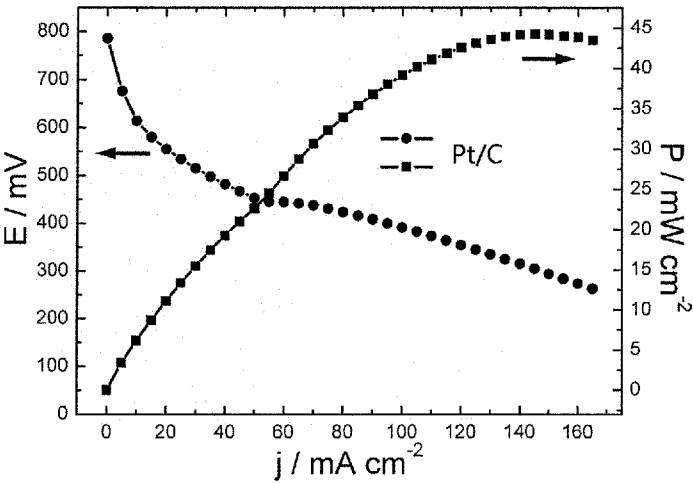


FIG.3

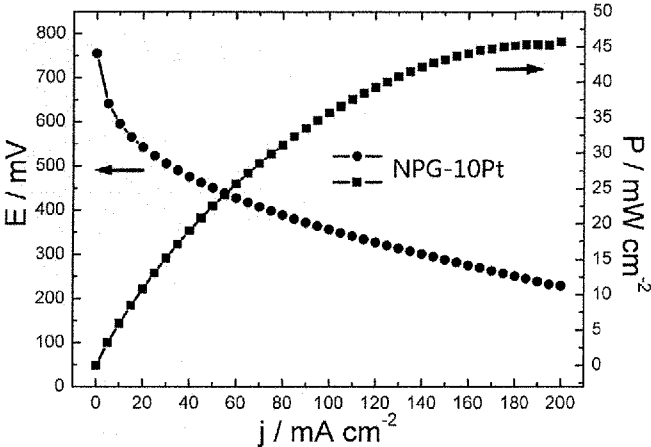


FIG.4

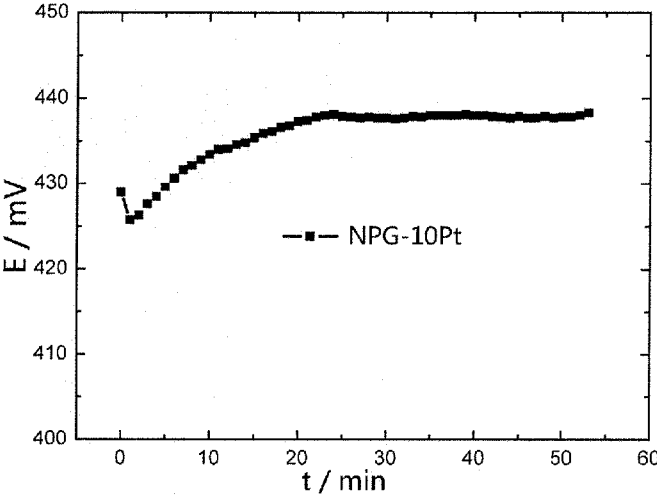


FIG.5

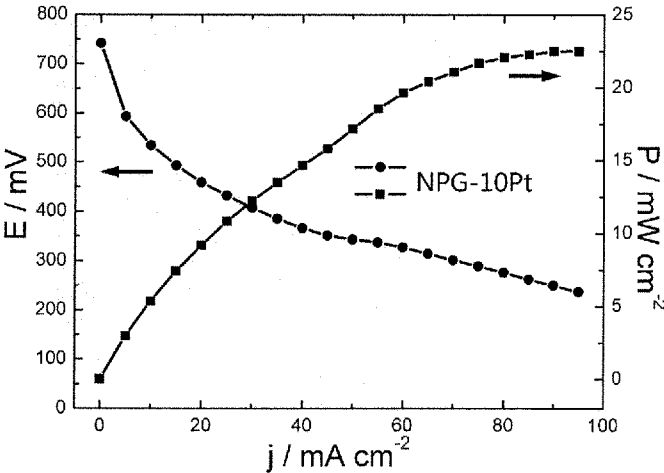


FIG.6

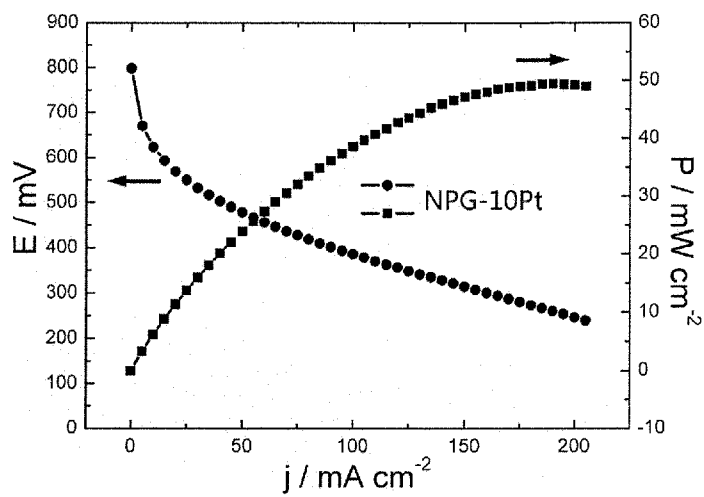


FIG. 7

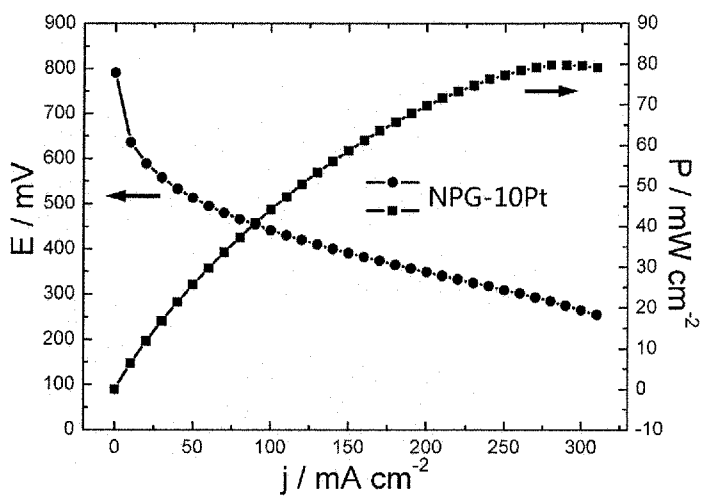


FIG. 8

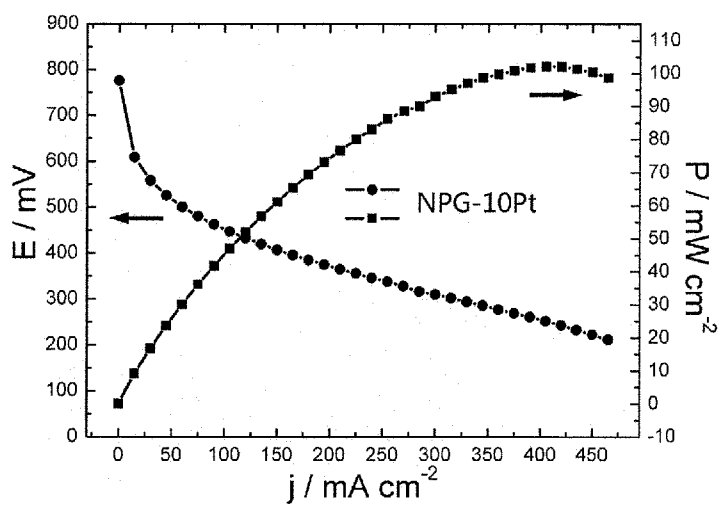


FIG. 9

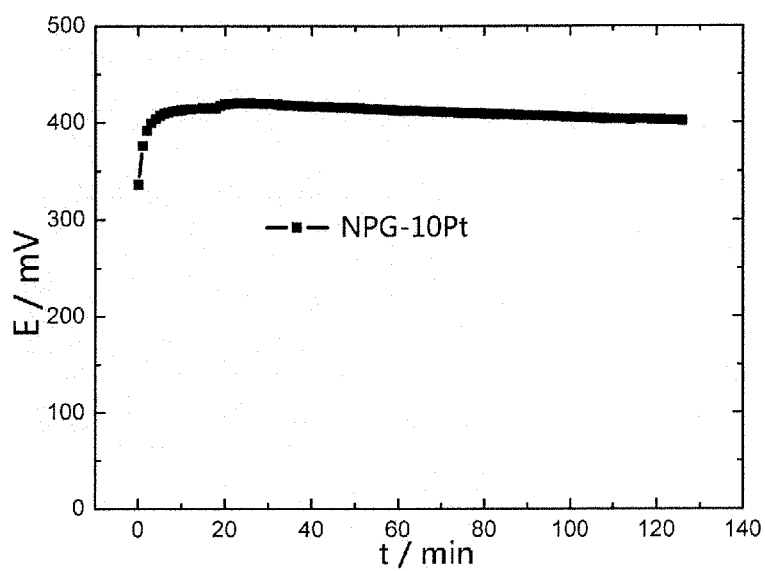


FIG.10

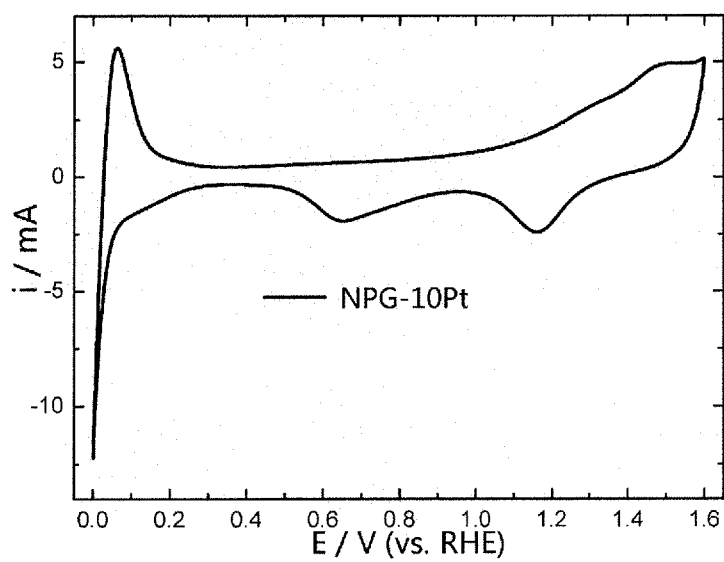


FIG.11

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 11/22535

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01M 8/10 (2011.01)

USPC - 429/483

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)

USPC — 429/483

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

USPC: 429/479,483-485,535 (text search limited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PubWEST (USPT, PGPB, JPAB, EPAB); Google (search terms below)

direct formic acid fuel cell, proton exchange membrane, anode, cathode, nanoporous, gold, platinum, silver, alloy, hot press, catalyst

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 7,632,779 B1 (Ding et al.) 15 Dec 2009 (15.12.2009), entire document especially Abstract, col 4, ln 55-60-2, col 7, ln 6-15, 5, ln 40-45, col 6, ln 30-35, col 8, ln 23-50, col 8, ln 23-30, col 5, ln 31-34, col 5, ln 3-15, col 6, ln 30-56 and col 8, ln 1-7	1-18
Y	US 2003/0118884 A1 (Hampden-Smith et al.) 26 Jun 2003 (26.06.2003), entire document especially Abstract, para [0015] and para [0200]	1-18
Y	US 6,720,106 B2 (Fukuda et al.) 13 Apr 2004 (13.04.2004), entire document especially Abstract, col 12, ln 50-65	13, 14 and 18

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


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"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

21 Mar 2011 (21.03.2011)

Date of mailing of the international search report

29 MAR 2011

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Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774