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(54) Title: A CATALYST FOR A FUEL CELL AND A METHOD FOR MAKING THE SAME

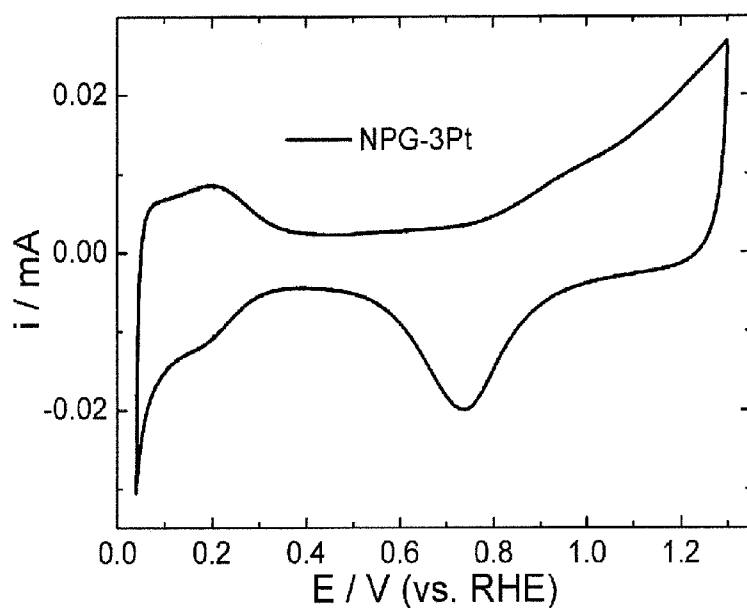


FIG.1

(57) Abstract: A catalyst for a fuel cell comprising: 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 (8) element, a group (10) element, a group (15) element, or a combination thereof, and a method of preparing a catalyst for a fuel cell comprising the steps of: immersing 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 in order to form an NPG-Pt article; and depositing either bismuth or ruthenium onto the surface of the NPG-Pt article resulting in either an NPG-Pt-Bi or NPG-Pt-Ru catalyst.

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A CATALYST FOR A FUEL CELL AND A METHOD FOR MAKING THE SAME

FIELD OF THE INVENTION

The invention belongs to the field of electrochemical technology, and relates to an efficient catalyst and a method for preparing the catalyst with nanoporous structure, in particular, relates to method for preparing a nanoporous gold (NPG) supported platinum surface alloy catalyst with a low platinum loading and high poisoning resistance for fuel cells.

BACKGROUD OF THE INVENTION

A fuel cell is an energy conversion device that converts the chemical energy of a fuel into electricity through reactions between the fuel and an oxidant with merits such as high efficiency of energy conversion and no pollution. The development of fuel cell technology is particularly urgent in light of the global energy crisis and serious environment pollution caused by traditional fossil fuels. Among various fuel cells, proton exchange membrane fuel cells (PEMFCs) with their low operating temperature and compact structure advantages are ideal as a power source for vehicles and other mobile devices. Direct liquid fuel cells, including direct methanol fuel cells and direct formic acid fuel cells, show significant advantages over hydrogen fuel cells in fuel supply. More specifically, direct formic acid 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 due to higher open circuit potential, and less fuel cross over.

At present, the high price is one of the key issues to inhibit the wide application of fuel cells. The fuel molecules are oxidized and oxygen is deoxidized on the catalyst in the

anode and cathode respectively to convert the chemical energy of the fuel into electrical energy. The fuel cell catalyst platinum with high price is the key issue of fuel cells' high price. 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, because the platinum catalyst nanoparticle is generally 2-4nm (it's very difficult to prepare smaller nanoparticle catalyst, and smaller catalyst will enter the small pores of support and to be useless), surface atoms proportion is less than 50% of total atoms, and will lose a lot when contact with the catalyst and support; 2) stability, as the catalyst and support connect only by physical adsorption, the catalyst aggregation or Ostwald ripening in the process of catalyst using will enlarge the catalyst particle, thus reducing the utilization of the catalyst, while the corrosion of carbon support also cause some loss of catalytic activity. (Z. W. Chen, M. Waje, W. Z. Li, Y. S. Yan, *Angew. Chem. Int. Ed.* 2007, 46, 4060.); 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 catalyst for a fuel cell and a method for making the same.

SUMMARY OF THE INVENTION

A catalyst for a fuel cell comprising: 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 8 element, a group 10 element, a group 15 element, or a combination thereof, and a method of preparing a catalyst for a fuel cell

comprising the steps of: immersing 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 in order to form an NPG-Pt article; and depositing either bismuth or ruthenium onto the surface of the NPG-Pt article resulting in either an NPG-Pt-Bi or NPG-Pt-Ru catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG.1 illustrates the full cyclic voltammetry (CV) curves of NPG-3Pt in 0.1M HClO₄.

FIG.2 illustrates the full cyclic voltammetry (CV) curves of NPG-3Pt in a mixed solution of 0.1M HClO₄ and 0.05M HCOOH.

FIG.3 illustrates the full cyclic voltammetry (CV) curves of NPG-3Pt-Bi catalyst in 0.1M HClO₄.

FIG.4 illustrates the full cyclic voltammetry (CV) curves of NPG-3Pt-Bi catalyst in a mixed solution of 0.1M HClO₄ and 0.05M HCOOH.

FIG.5 illustrates the full cyclic voltammetry (CV) curves of NPG-Pt catalyst in 0.5M H₂SO₄.

FIG.6 illustrates the full cyclic voltammetry (CV) curves of NPG-Pt catalyst in a mixed solution of 0.5M H₂SO₄ and 1M CH₃OH.

FIG.7 illustrates the full cyclic voltammetry (CV) curves of NPG-Pt-Ru catalyst in 0.5M H₂SO₄.

FIG.8 illustrates the full cyclic voltammetry (CV) curves of NPG-Pt-Ru catalyst in a mixed solution of 0.5M H_2SO_4 and 1M CH_3OH .

FIG.9 illustrates the full cyclic voltammetry (CV) curves of NPG-Pt64 in 0.1M HClO_4 .

FIG.10 illustrates the full cyclic voltammetry (CV) curves of NPG-Pt64 catalyst in a mixed solution of 0.1M HClO_4 and 1M HCOOH .

FIG.11 illustrates the full cyclic voltammetry (CV) curves of NPG-Pt64-Bi catalyst in 0.1M HClO_4 .

FIG.12 illustrates the full cyclic voltammetry (CV) curves of NPG-Pt64-Bi catalyst in the mixed solution of 0.1M HClO_4 and 1M HCOOH .

DETAILED DESCRIPTION

The present invention is to provide catalysts based on nanoporous gold (NPG) and methods of preparing catalysts for fuel cells, in particular, to provide nanoporous gold supported platinum surface alloy catalysts with low precious metal loading and high poisoning resistance.

In order to improve the catalytic activity of a platinum catalyst, one solution is to alloy platinum with some other metal atoms like palladium, bismuth or ruthenium, or to 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 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 electricity catalyst support, because of superior properties such as three dimensional nanostructure, continuous pore structure and pore wall, good electrical conductivity, high surface area, and strong corrosion resistance. Karl Sieradzki and R. C. Newman reported a method of forming porous gold structure by electrochemical etching the gold-silver alloy in 1990.(K. Sieradzki, R. C. Newman "Micro- and Nano-porous Metallic Structures" US Patent, 4,977,038, Dec. 11, 1990). Several methods have been reported by one of the inventors to deposit catalytic active metals such as platinum on nanoporous gold (NPG) in highly controllable ways. (1. "Method of Plating Metal Leafs and Metal Membranes" Worldwide Patent, WO 2004/021481, Nov. 3, 2004; 2. CN 101332425; 3. CN 101332438 B).

Compared to the carbon supported platinum catalyst, the nanoporous gold supported platinum catalyst has the following advantages: 1) the nanoporous metal has a three dimensional, bi-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.

In a liquid fuel cell, the oxidation of small organic molecules of fuel (methanol, formic acid, ethanol, acetic acid, dimethyl ether, etc) should be catalyzed by platinum which is similar to a hydrogen fuel cell. However, unlike hydrogen oxidation in a hydrogen fuel cell, the oxidation of small organic molecules in a liquid fuel cell is slow even when catalyzed by platinum, as a poisoning intermediate could be readily formed and inhibit the

reaction. For example, the oxidation reaction of methanol on catalytic platinum produces a carbon monoxide intermediate which may be firmly adsorbed on the surface of the catalyst which poisons the catalyst. Also the oxidation reaction of formic acid on platinum will produce a carbon monoxide intermediate product which poisons the catalyst. Therefore a liquid fuel cell anode needs a large amount of catalyst to overcome the over-potential caused by the low catalytic activity and poisoning. Extensive research shows that alloying platinum with other metals or adsorbing an additional metal onto the platinum can greatly reduce the catalyst poisoning during the oxidation of small organic molecules. The poisoning resistance achieved by adding other metals are as follows: 1) accelerate the removal of the carbon monoxide poisoning intermediate through a bi-functional mechanism; 2) improve the catalytic activity of platinum by altering the electronic structure; 3) reduce the poisoning intermediate formation by changing the atomic ensemble of platinum and the path of the reaction. Recent research has shown that a sub-monolayer of gold deposited on to the surface of an NPG supported Pt catalyst by an under potential deposition (UPD) combined with replacement reaction can improve the catalytic activity of formic acid. (Y. Ding, R. Y. Wang, "Method of Preparing a Catalyst for Direct Formic Acid Fuel Cells" US 7,632,779 B1, Dec. 15, 2009). However, the sub-monolayer gold could only change the ensemble size of platinum. The catalytic activity improvement is limited to formic acid electrooxidation and is not effective for the oxidation of other small organic molecules.

In order to solve the poisoning problem of an NPG supported platinum catalyst, the present invention prepares the NPG supported platinum surface alloy catalyst using a surface modification method. The NPG supported platinum surface alloy catalyst not only maintains the advantages of an NPG supported platinum catalyst such as good electrical conduction, high platinum utilization and good stability; it also solves the problem of catalyst poisoning.

The present invention shows that, the methods of preparing a NPG supported platinum catalyst after de-alloying gold and silver alloys to get the nanoporous gold include: 1) surface ion adsorption combined with electrochemical reduction, or 2) under potential deposition (UPD) combined with in-situ replacement, or 3) the platinum deposited on nanoporous gold surface using hydrazine vapor reduction method to form the catalyst. Then immersing the nanoporous gold supported platinum catalyst in a certain concentration of bismuth or ruthenium solution by adding some potential for a certain time (or soak for a certain time) to deposit bismuth or ruthenium onto the surface of the NPG supported platinum catalyst. The present invention controls a catalyst's catalytic activity by adjusting the platinum loading by methods of: a) regulating the cycles of adsorption deposition, b) regulating the cycles of UPD combined with in-situ replacement, or c) regulating the time of reduction in hydrazine vapor; and adjusting the bismuth or ruthenium loading by regulating the deposition potential and deposition time (or soaking time).

A. DEFINITIONS

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 “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 “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-3Pt”, as used herein, refers to an NPG with three deposition cycles 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 catalyst from the open circuit potential to 0.3V (versus standard hydrogen electrode) by 50mV/s three times according to the present invention resulting in an NPG-3 Pt catalyst.

The term “NPG-3Pt-Bi”, as used herein, refers to an NPG-3Pt 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-3Pt catalyst at 0.2V (versus standard hydrogen electrode) for 400 seconds according to the present invention resulting in an NPG-3 Pt-Bi catalyst.

The term “NPG-Pt”, 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, 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 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-Pt catalyst.

The term “NPG-Pt-Ru”, as used herein, refers to an NPG-Pt catalyst with a layer of ruthenium deposited onto its surface by copper (Cu) under potential deposition (UPD). In

one embodiment of the present invention, ruthenium is deposited onto the surface of an NPG-Pt catalyst at 0.2V (versus standard hydrogen electrode) for 400 seconds according to the present invention resulting in an NPG-1Pt-Ru 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 "Group 8 elements", as used herein, includes iron, ruthenium and osmium. 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.

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.

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 or Ru) 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 or ruthenium has thickness of 0.0025-0.5nm. Additionally, different atomic layers of bismuth or ruthenium have corresponding bismuth or ruthenium loading. In one embodiment of the present invention, a 0.01-0.99 atomic layer bismuth or ruthenium has thickness of about 0.25nm, because bismuth and ruthenium each have a certain atomic radius, a 0.05 atomic layer of bismuth or ruthenium still has a thickness of each atomic radius respectively. In another embodiment of the present invention, the loading of either bismuth or ruthenium does not reach one atomic layer, that is to say, neither bismuth nor ruthenium cover the NPG completely. In still another embodiment of the present invention, the 0.01-0.99 atomic layer of either bismuth or ruthenium 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 catalyst for a fuel cell comprising a nanoporous gold having one or more coatings of one or more additional metals selected from the group comprising: a group 8 element, a group 10 element, a group 15 element, or a combination thereof on its surface. In one embodiment of the present invention, the Group 8 elements include ruthenium, the Group 10 elements include platinum and the

Group 15 elements include bismuth. In another embodiment of the present invention, the catalyst for a fuel cell includes a 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 or less than one layer of ruthenium bonded to the surface of the platinum. In yet another embodiment of the present invention, the catalyst 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; 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 or a layer of ruthenium 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 discloses another catalyst for a fuel cell comprising: a nanoporous gold having one or more coatings of one or more additional metals selected from the group comprising: a group 8 element, a group 10 element, a group 11 element, a group 15 element, or a combination thereof on its surface. In one embodiment of the present invention, the group 8 elements include ruthenium, 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 catalyst for a fuel cell is 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 either bismuth or ruthenium bonded to the surface of the platinum. In yet another embodiment of the present invention, the catalyst 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; 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 or a layer of ruthenium atoms having a coverage of 0.01-0.99 bonded to the layer of platinum. In yet another embodiment, the catalyst for a fuel cell may be an anode catalyst.

In one embodiment of the present invention, a catalyst may be an NPG-Pt-Bi catalyst or an NPG-Pt-Ru 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 μm 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 μm , 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 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-Pt5-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 one embodiment of the present invention, the anode catalyst may be a catalyst ranging from a NPG-Pt1-Ru to a NPG-Pt1000-Ru. In another embodiment, the anode catalyst may be a catalyst ranging from a NPG-Pt1-Ru to a NPG-Pt500-Ru. In still another embodiment, the anode catalyst may be a catalyst ranging from a NPG-Pt 5-Ru to a NPG-Pt100-Ru. In yet another embodiment, the anode catalyst may be a catalyst ranging from a NPG-Pt10-Ru to a NPG-Pt50-Ru. In another embodiment, the anode catalyst may be a NPG-Pt64-Ru catalyst. In still another embodiment, the anode catalyst may be a NPG-Pt16-Ru catalyst. In yet another embodiment, the anode catalyst may be a NPG-Pt8-Ru 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-100Pt-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-3Pt-Bi catalyst. In yet another embodiment, the anode catalyst may be a NPG-1Pt-Bi catalyst.

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

The present invention also discloses a method of preparing a catalyst for a fuel cell 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 either bismuth or ruthenium onto the surface of the NPG-Pt article resulting in a catalyst, and more specifically an NPG-Pt-Bi catalyst or an NPG-Pt-Ru catalyst.

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 combined with 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 ion or ruthenium ion to form the Bi-modified or Ru-modified nanoporous gold catalyst supported platinum catalyst.

In order to form the nanoporous gold or nanoporous gold membrane, 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 μm thick, and 10-60% gold (wt.%). In another embodiment of the present invention, the gold-silver alloy article may have a thickness of 100nm-1 μm , 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 combined with electrochemical reduction method; (2) an under potential deposition method combined with in-situ replacement; (3) a chloroplatinic ion 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 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 and deposit directly 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 1 and 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 or ruthenium 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 or ruthenium is deposited onto the surface of a NPG-Pt article by placing the NPG-Pt article into a perchloric acid solution containing 0.1 – 100mM bismuth or ruthenium 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 or an NPG-Pt-Ru catalyst. In another embodiment of the present invention, bismuth or ruthenium is deposited onto the surface of a NPG-Pt article by placing the NPG-Pt article into a perchloric acid solution containing 0.1 – 100mM bismuth or ruthenium and soaking the NPG-Pt article for a soaking time period of 1-1000 minutes to obtain an NPG-Pt-Bi catalyst or an NPG-Pt-Ru catalyst. In yet another embodiment of the above method, the concentration of the chloroplatinic ion or chloroplatinous ion solution is 0.5-5mM. In still

another embodiment of the above method, the concentration of the perchloric acid solution containing Bi or Ru 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.

The present invention also describes another method of preparing a catalyst for a fuel cell comprising the steps of: immersing 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 one or more additional metals onto the surface of the NPG, where the additional metals are selected from the group comprising: a group 8 element, a group 10 element, a group 15 element, or a combination thereof; and the layers of additional metals range in thickness from sub-monoatomic to a plurality of monoatomic or atomic layers in order to form the catalyst.

In one embodiment of the above method, the group 8 elements include ruthenium; the group 10 elements include palladium and platinum and the group 15 elements include bismuth. In another embodiment of the above method, the catalyst is 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 either bismuth or ruthenium, bonded to the surface of the nanoporous gold and/or the platinum. In yet another embodiment of the above method, the 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 and a layer of bismuth or ruthenium having a coverage of 0.01-0.99 bonded to the nanoporous gold and/or the layer of platinum.

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 cycle of adsorption deposition, ii) regulating the cycle 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 or ruthenium loading by regulating the deposition potential and deposition time period (or soaking time period).

According to the embodiments of the present invention, the advantages of the methods disclosed are as follows:

(1) The method of depositing sub-monoatomic layer of bismuth or ruthenium on the surface of nanoporous gold supported platinum catalyst uses electrochemical or adsorption deposition. It is simple, controllable, and can control the catalytic activity of catalyst by easily regulating the deposition potential and deposition time to adjust the bismuth or ruthenium loading.

(2) The methods prepare a highly efficient catalyst with low precious metal loading for a fuel cell, providing advantages such as good conductivity, good stability, high platinum utilization and low precious metal loading of a nanoporous gold supported platinum catalyst, while avoiding the disadvantages of poisoning and poor catalytic activity of a nanoporous gold supported Platinum catalyst.

When comparing traditional catalyst supported by carbon to the catalysts made by the methods described in the present invention, the advantages of either Bi-modified or Ru-modified NPG-Pt catalysts with low precious metal loading for direct formic acid fuel cell anode include the following:

(1) NPG has superior electron transfer ability and superior chemical and electrochemical corrosion resistance than a traditional fuel cell catalyst;

(2) The three dimensional structure of NPG can make it much easier for the reactant to reach the surface of electrode;

(3) NPG can easily be made into a membrane structure which is compatible with the fuel cell electrolyte membrane, thus NPG is a better catalyst support.

(4) A platinum catalyst can be bonded to the surface of NPG with a sub-atomic layer or a plurality of atomic layers by methods which include i) surface ion adsorption combined with electrochemical reduction, or ii) under potential deposition (UPD) combined with in-situ replacement, or iii) reduction in hydrazine vapor, greatly improving the utilization of platinum catalyst;

(5) The addition of a sub-atomic layer of bismuth or ruthenium on the surface of an NPG-Pt improves the catalytic activity by adjusting the reaction route of the formic acid oxidation reaction, changing the atomic structure, and providing a dual-channel mechanism.

(6) A Bi-modified or Ru-modified NPG-Pt catalyst can decrease the precious metal loading by about an order of magnitude while maintaining the same discharge level, and also decrease the platinum loading by about two orders of magnitude

C. EXAMPLES

Example 1

1) A 9K gold-silver alloy sample (1.2 cm long, 1 cm wide, 100 nm thick) was placed in concentrated nitric acid for 120 minutes at 20°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 solution for 5 minutes followed by a cleaning in deionized water. Platinum was then deposited onto the surface of the NPG

using the electrochemical reduction method. This process is repeated 3 times to obtain a NPG-3Pt catalyst.

3) The NPG-3Pt catalyst was placed in 0.1M HClO₄ solution containing 3mM bismuth (Bi), in order to deposit Bi onto the surface of the NPG-3Pt catalyst by soaking for 5 minutes to form a NPG-3Pt-Bi catalyst. The full CV curves of NPG-3Pt-Bi catalyst were shown in FIG.3 and the electrochemical catalytic activity of NPG-3Pt-Bi catalyst for HCOOH was shown in FIG.4.

FIG.1 illustrates the full cyclic voltammetry (CV) curves of an NPG-3Pt catalyst in 0.1M HClO₄, 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 3 times to obtain the NPG-3Pt. The curve shows that, the platinum begins to oxidize around 0.8V, the platinum reduction peak is around 0.75V during the backward scan, and hydrogen under potential adsorption-desorption peaks at the platinum surface are between 0.05-0.4V. It is clear that the platinum has been deposited onto the surface of the nanoporous gold.

FIG.2 illustrates the full cyclic voltammetry (CV) curves of NPG-3Pt catalyst in a mixed solution of 0.1M HClO₄ and 0.05M HCOOH. The HCOOH oxidation starting peak position and the oxidation peak position are relatively low, which shows the adsorption depositing samples have high catalytic activity and good poisoning resistance.

FIG.3 illustrates the full cyclic voltammetry (CV) curves of an NPG-3Pt-Bi catalyst in 0.1M HClO₄, 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 3 times to obtain the NPG-3Pt, followed by once deposition of Bi onto the surface of the platinum. The curves show that, after the

deposition of Bi, the hydrogen under potential adsorption-desorption peaks were partially covered by the deposition of Bi, and the oxidation peak of Bi at 0.9V shows that Bi has been successfully deposited on the NPG-3Pt catalyst.

FIG.4 illustrates the full cyclic voltammetry (CV) curves of an NPG-3Pt-Bi catalyst in a mixed solution of 0.1M HClO₄ and 0.05M HCOOH. Compared with the sample not modified with Bi (FIG.2), the HCOOH oxidized at lower potential, and the oxidant current also increased, which shows improved catalytic performance after being modified with Bi resulting in increased catalytic activity and improved poisoning resistance.

Example 2

- 1) A 12K gold-silver alloy sample (1.2 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) Platinum was deposited onto the surface of the NPG by a single round of copper UPD and platinum replacement to obtain an NPG-Pt catalyst;
- 3) The NPG-Pt catalyst was placed in a mixed solution of 1mM ruthenium and 0.1M HClO₄ and soaked for 10 seconds in order to deposit Ru onto the surface of the NPG-Pt catalyst to form a NPG-Pt-Ru catalyst with low precious metal loading for fuel cell. The full CV curves of NPG-Pt-Ru catalyst were shown in FIG.7 and the electrochemical catalytic activity of NPG-Pt-Ru catalyst for CH₃OH was shown in FIG.8.

FIG.5 illustrates the full cyclic voltammetry (CV) curves of an NPG-Pt catalyst in 0.5M H₂SO₄, which was made by de-alloying a 12 karat (K), 100 nm thick Ag-Au alloy in 68%(wt.%) nitric acid for 30 min at 30°C resulting in an NPG, followed by subjecting the NPG to under potential deposition(UPD) of copper (Cu) and platinum replacement. The curve shows that, the platinum begins to oxidize around 0.8V, the platinum reduction peak

is around 0.75V during the backward scan, and hydrogen under potential adsorption-desorption peaks at the platinum surface are between 0.05-0.4V. It is clear that the platinum has been deposited onto the surface of the nanoporous gold. Additionally, the very small gold reduction peak around 1.2V shows that the gold was almost completely covered by platinum.

FIG.6 illustrates the full cyclic voltammetry (CV) curves of an NPG-Pt catalyst in a mixed solution of 0.5M H_2SO_4 and 1M CH_3OH which was made by de-alloying a 12 karat (K), 100 nm thick Ag-Au alloy in 68%(wt.%) nitric acid for 30 min at 30°C resulting in an NPG, followed by subjecting the NPG to under potential deposition(UPD) of copper (Cu) and platinum replacement. The curves show that the CH_3OH oxidation onset potential is around 0.6V and the large current density, normalized to the platinum quality, shows the high utilization of platinum.

FIG.7 illustrates the full cyclic voltammetry (CV) curves of an NPG-Pt-Ru catalyst in 0.5M H_2SO_4 , which was prepared by de-alloying a 12 karat (K), 100 nm thick Ag-Au alloy in 68%(wt.%) nitric acid for 30 min at 30°C resulting in an NPG, followed by subjecting the NPG to under potential deposition(UPD) of copper (Cu) and platinum replacement followed by once deposition of ruthenium. The curves show that around 0.05-0.4V the hydrogen under potential adsorption-desorption peaks become decrescent, around 0.4-0.6V the electric double layer grows wider and the oxidation peak becomes large. This shows that ruthenium has been successfully deposited onto the surface of the platinum.

FIG.8 illustrates the full cyclic voltammetry (CV) curves of an NPG-Pt-Ru catalyst in a mixed solution of 0.5M H_2SO_4 and 1M CH_3OH , which was prepared by de-alloying a 12 karat (K), 100 nm thick Ag-Au alloy in 68%(wt.%) nitric acid for 30 min at 30°C resulting in

an NPG, followed by subjecting the NPG to under potential deposition(UPD) of copper (Cu) and platinum replacement followed by once deposition of ruthenium. The curves show that the methanol oxidation peak is around 0.5V, though the current density normalized to platinum quality decreases, the methanol starting peak position is forward about 100mV. This shows the nanoporous gold supported platinum catalyst modified with ruthenium has higher catalytic activity and higher carbon monoxide poisoning resistance capability in the process of methanol oxidation.

FIG.9 illustrates the full cyclic voltammetry (CV) curves of a sample in 0.1M HClO₄, where the sample has an NPG-Pt64 catalyst which was made by de-alloying a 12 karat (K), 100 nm thick Ag-Au alloy in 68%(wt.%) nitric acid for 15 min at 30°C resulting in an NPG, followed by placing the NPG in a 1g/L H₂PtCl₆ solution (pH value is 10), in order to deposit platinum onto the surface of the NPG in N₂H₄ vapor for 64 minutes to form an NPG-Pt64 catalyst. The curve shows that the platinum begins to oxidize around 0.8V, the platinum reduction peak is around 0.8V during the backward scan, and hydrogen under potential deposition (UPD) adsorption-desorption peaks at the platinum surface are between 0.05-0.4V. This shows that platinum has been successfully deposited onto the surface of the NPG.

FIG.10 illustrates the full cyclic voltammetry (CV) curves of a platinum decorated NPG(NPG-Pt64) catalyst in a mixed solution of 0.1M HClO₄ and 1M HCOOH where the currents have been normalized to the geometrical areas of the samples. The small oxidation current during the forward scan compared to the backward scan peaks shows the NPG-Pt64 catalyst would be easily poisoned by CO.

Example 3

1) A 12K gold-silver alloy sample (1.2 cm long, 1 cm wide, 100 nm thick) was immersed in concentrated nitric acid for 15 minutes to selectively dissolve silver from the alloy 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=10), in order to deposit platinum onto the surface of the NPG in N_2H_4 vapor for 64 minutes resulting in an NPG-Pt64 catalyst;

3) The NPG-Pt64 catalyst was placed in 0.1M HClO_4 solution containing 3mM bismuth (Bi), in order to deposit Bi onto the surface of the NPG-Pt64 catalyst by adding 0.4V potential (versus standard hydrogen electrode) for 400 seconds to form a NPG-Pt64-Bi catalyst. The full CV curves of the NPG-Pt64-Bi catalyst are shown in FIG.11 and the electrochemical catalytic activity of the NPG-Pt64-Bi catalyst for HCOOH is shown in FIG.12.

FIG.11 illustrates the full cyclic voltammetry (CV) curves of the Bi-modified nanoporous gold supported platinum catalyst (NPG-Pt64-Bi) in 0.1M HClO_4 . The catalyst was made by under potential depositing (UPD) Bi on the surface of the nanoporous gold supported platinum at 0.4V (versus standard hydrogen electrode) for 400 seconds. The curve shows that hydrogen UPD adsorption-desorption peaks were covered by the deposition of Bi. The Bi oxidation peak at 1V and the reduction peak at 0.4V shows that Bi has been deposited on the nanoporous gold supported platinum catalyst successfully to form the Bi-modification nanoporous gold supported platinum catalyst (NPG-Pt64-Bi).

FIG.12 illustrates the full cyclic voltammetry (CV) curves of a sample with an NPG-Pt64-Bi catalyst in a mixed solution of 0.1M HClO_4 and 1M HCOOH , where the currents have been normalized to the geometrical areas of the samples. The higher

oxidation current during the forward scan and backward scan compared to the NPG-Pt64 catalyst show that the NPG-Pt64-Bi catalyst displays higher catalytic activity. The almost coincident oxidation current during the forward scan compared to the backward scan peaks shows that the NPG-Pt64-Bi catalyst would not be easily poisoned by CO.

Example 4

1) A 12K gold-silver alloy sample (1.3 cm long, 1 cm wide, 1 μ m 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 a 1mM H_2PtCl_6 solution for 5 minutes for adsorbing followed by a cleaning in deionized water. Platinum was then deposited onto the surface of the NPG using the electrochemical reduction method. This process is repeated 10 times to obtain a NPG-10Pt catalyst.

3) The NPG-10Pt catalyst was placed in 0.1M HClO_4 solution containing 3mM bismuth (Bi) in order to deposit Bi onto the surface of the NPG-10Pt catalyst by adding 0.4V potential (versus standard hydrogen electrode) for 400 seconds to form a NPG-10Pt-Bi catalyst with low precious metal loading for fuel cell.

WHAT IS CLAIMED IS

1. A catalyst for a fuel cell comprising:
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 8 element, a group 10 element, a group 15 element, or a combination thereof.
2. The catalyst for a fuel cell of claim 1 wherein, said group 8 elements being ruthenium; said group 10 elements being palladium and platinum; and said group 15 elements being bismuth.
3. The catalyst for a fuel cell of claim 1 wherein said 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 either bismuth or ruthenium, bonded to the surface of said nanoporous gold and/or said platinum.
4. The catalyst for a fuel cell of claim 1 wherein said 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 and a layer of bismuth atoms or ruthenium atoms bonded to said nanoporous gold and/or said layer of platinum;
said layer of bismuth or ruthenium having a coverage of 0.01-0.99.

5. The catalyst for a fuel cell of claim 1 wherein said catalyst being an anode catalyst.

6. The catalyst for a fuel cell of claim 1 wherein said Group 8 element having a thickness of less than 10nm said Group 10 element having a thickness of less than 500nm and said Group 15 element having a thickness of less than 20nm.

7. A method of preparing a catalyst for a fuel cell 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; and
depositing bismuth onto the surface of the NPG-Pt article resulting in an NPG-Pt-Bi catalyst; or
depositing ruthenium onto the surface of the NPG-Pt article resulting in an NPG-Pt-Ru catalyst.

8. The method according to claim 7 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.%).

9. The method according to claim 7 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.

10. The method according to claim 7 wherein said layer of platinum being deposited onto said NPG using a method selected from the group comprising: (1) a surface ion adsorption combined with 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.

11. The method according to claim 10 wherein for option (1) 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 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 1 and 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.

12. The method according to claim 7 wherein either bismuth or ruthenium are deposited onto the surface of the NPG-Pt article by:

placing said NPG-Pt article into a perchloric acid solution containing either bismuth or ruthenium, and adding a 0-0.5V potential (versus standard hydrogen electrode) to said NPG-Pt article for a deposition time period of 0.1-1000 minutes to obtain either an NPG-Pt-Bi or an NPG-Pt-Ru catalyst; or

placing said NPG-Pt article into a perchloric acid solution containing bismuth or ruthenium and soaking said NPG-Pt article for a soaking time period of 0.1-1000 minutes to obtain either an NPG-Pt-Bi or an NPG-Pt-Ru catalyst.

13. The method according to claim 7 wherein said gold-silver alloy article having a thickness of 0.1-1 μ m, a width of 1-10cm, and a length of 2-15cm, and comprising 50% gold (wt.%).

14. The method according to claim 9 wherein said gold-silver alloy article being immersed in concentrated nitric acid for a time period ranging from 15 to 60 minutes.

15. The method according to claim 11 wherein the concentration of said chloroplatinic ion or chloroplatinous ion solution in option (1) being 0.5-5mM, the soaking time in chloroplatinic ion or chloroplatinous ion solution is preferably 3-30 minutes, the cleaning step is preferably 3-6 times.

16. The method according to claim 11 wherein the concentration of said chloroplatinic ion solution in option (3) 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.

17. The method according to claim 12, wherein the concentration of said perchloric acid solution containing Bi or Ru 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 5-10minutes.

18. A method of preparing a catalyst for a fuel cell 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 one or more additional metals onto the surface of said NPG;
said additional metals being selected from the group comprising: a group 8 element being ruthenium, a group 10 element being palladium and platinum, a group 15 element being bismuth, or a combination thereof; and
said layers of additional metals ranging in thickness from sub-monoatomic to a plurality of monoatomic or atomic layers in order to form said catalyst.

19. The method according to claim 17 wherein said 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 either bismuth or ruthenium, bonded to the surface of said nanoporous gold and/or said platinum.

20. The method according to claim 17 wherein said 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 and a layer of bismuth atoms or ruthenium atoms bonded to said nanoporous gold and/or said layer of platinum;

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

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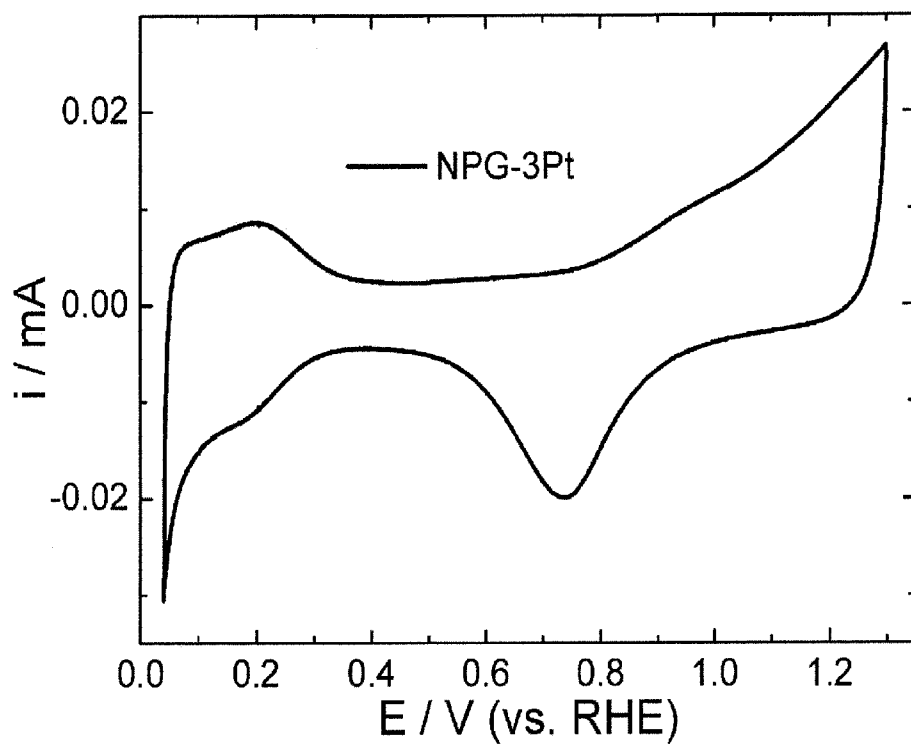


FIG.1

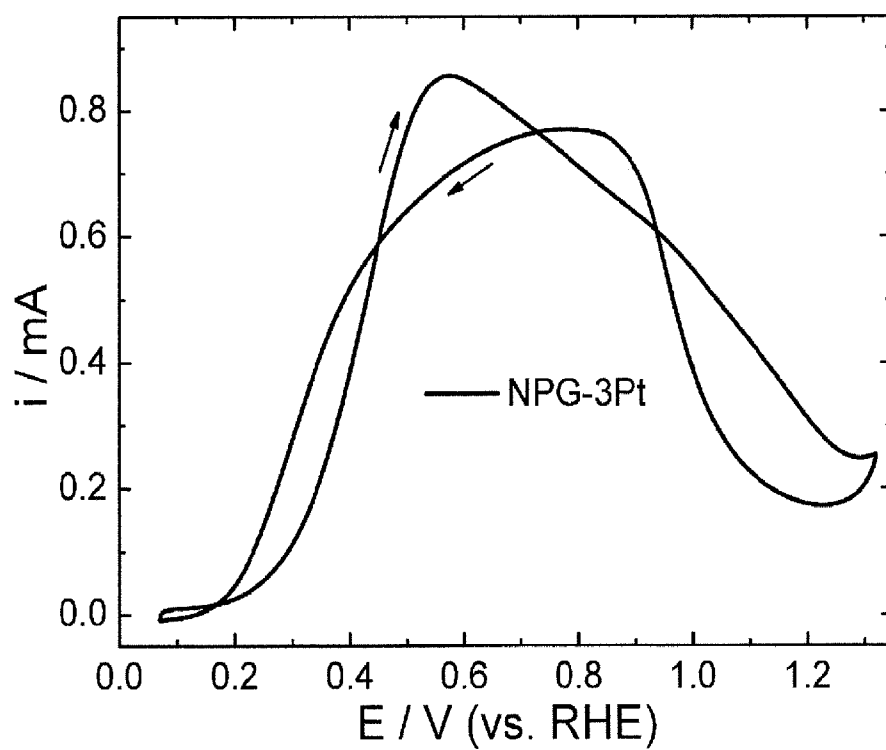


FIG.2

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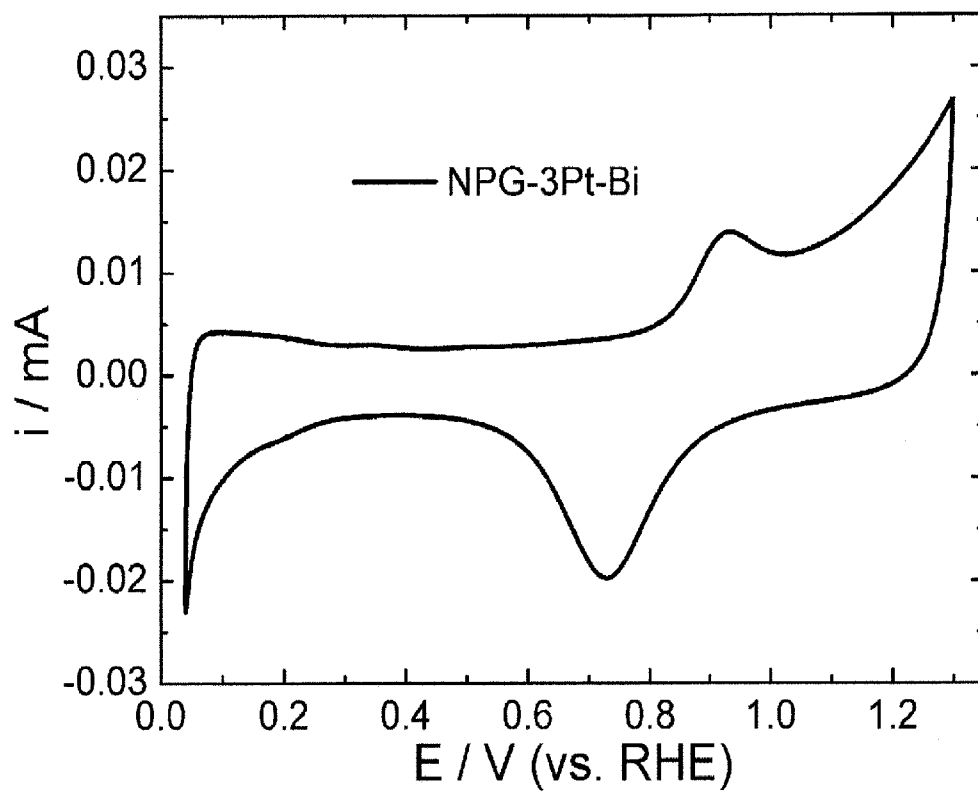


FIG.3

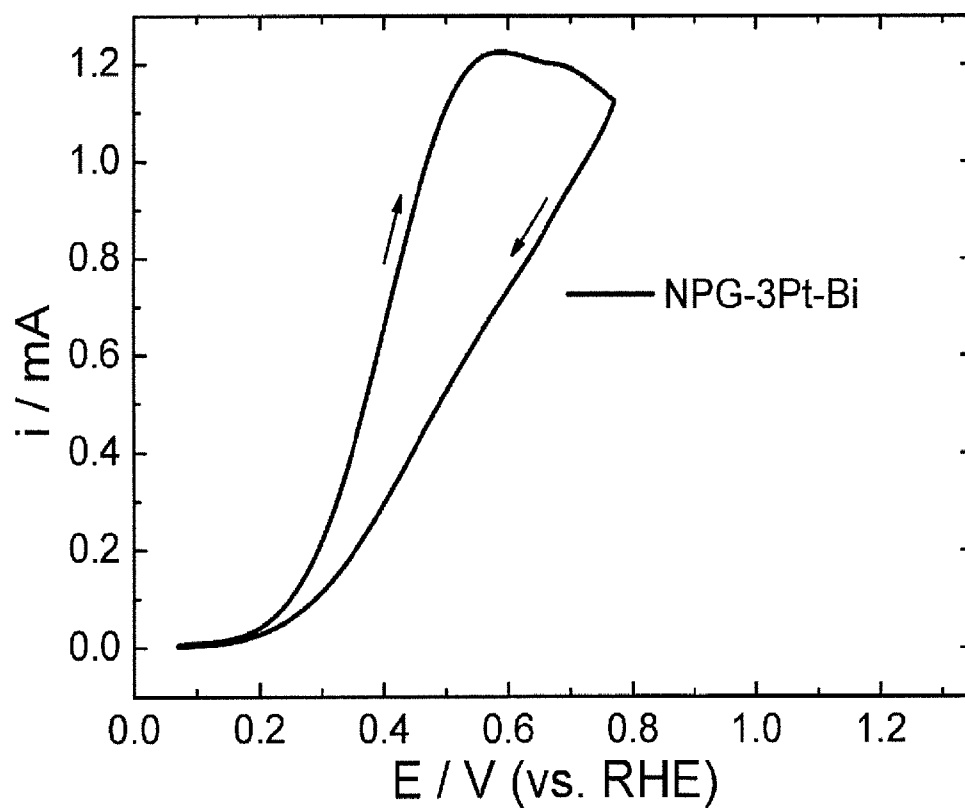


FIG.4

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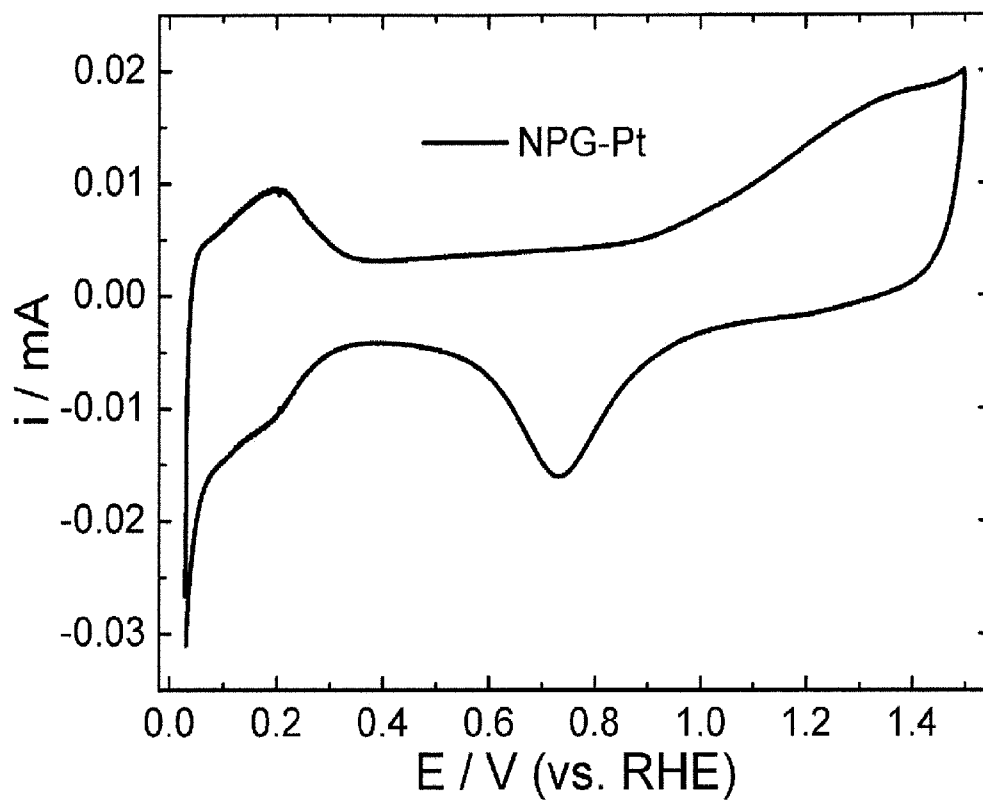


FIG.5

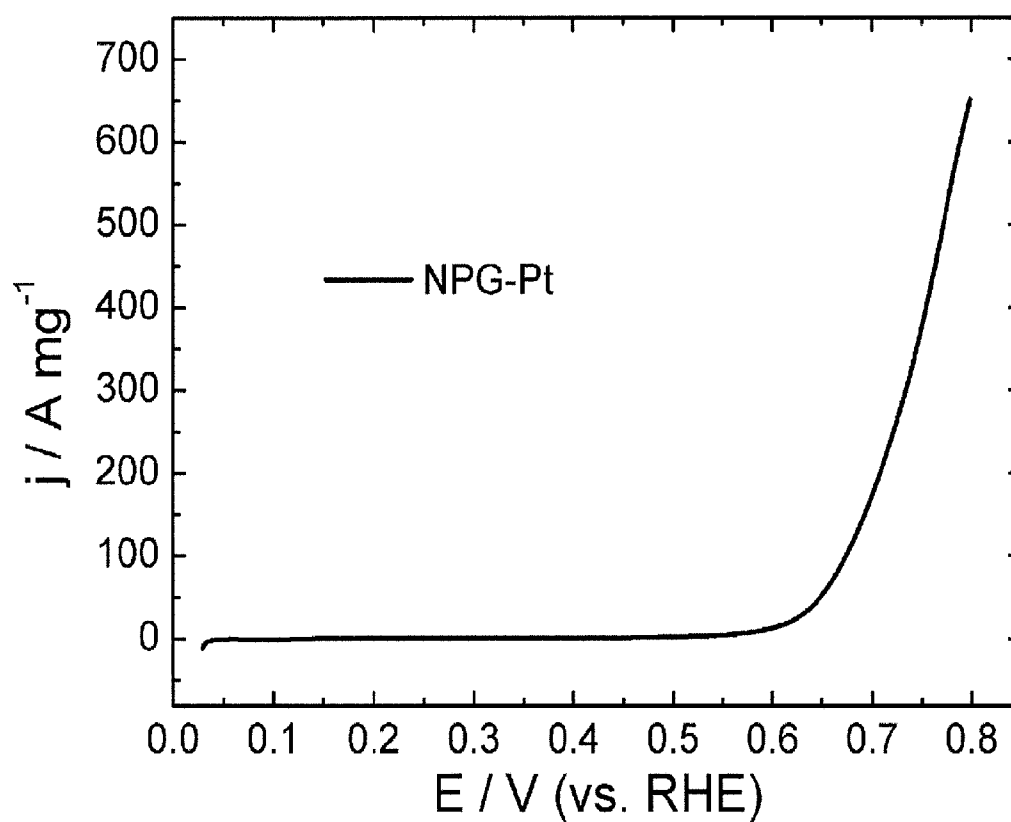


FIG.6

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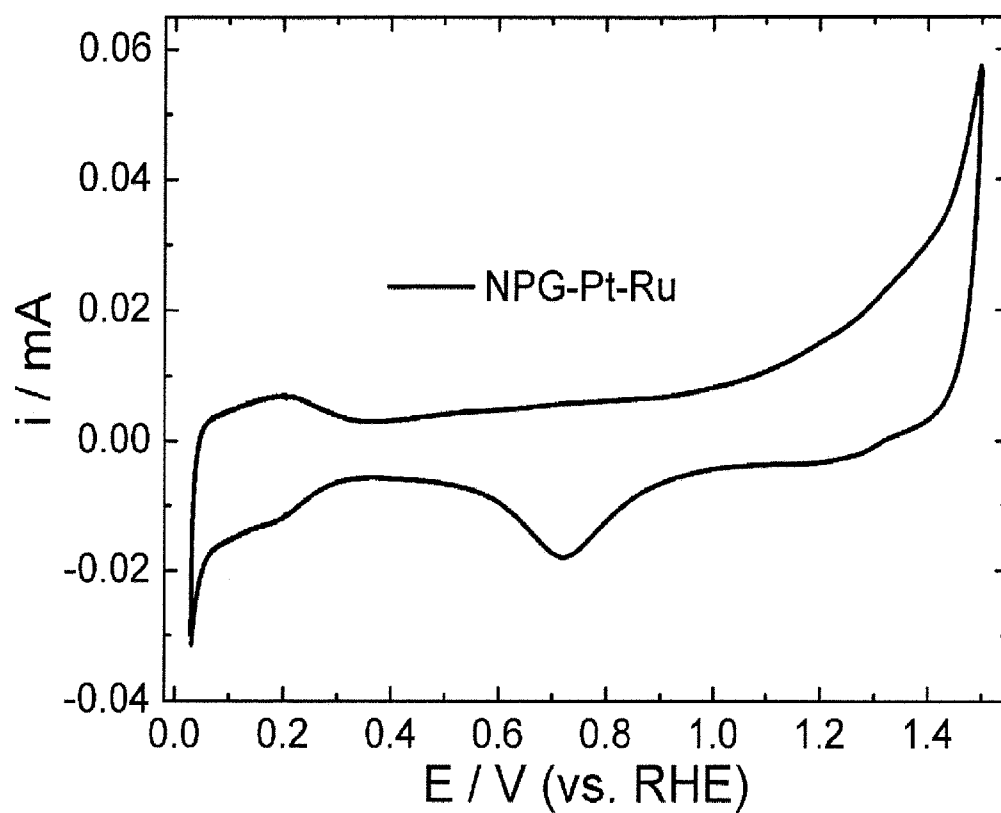


FIG.7

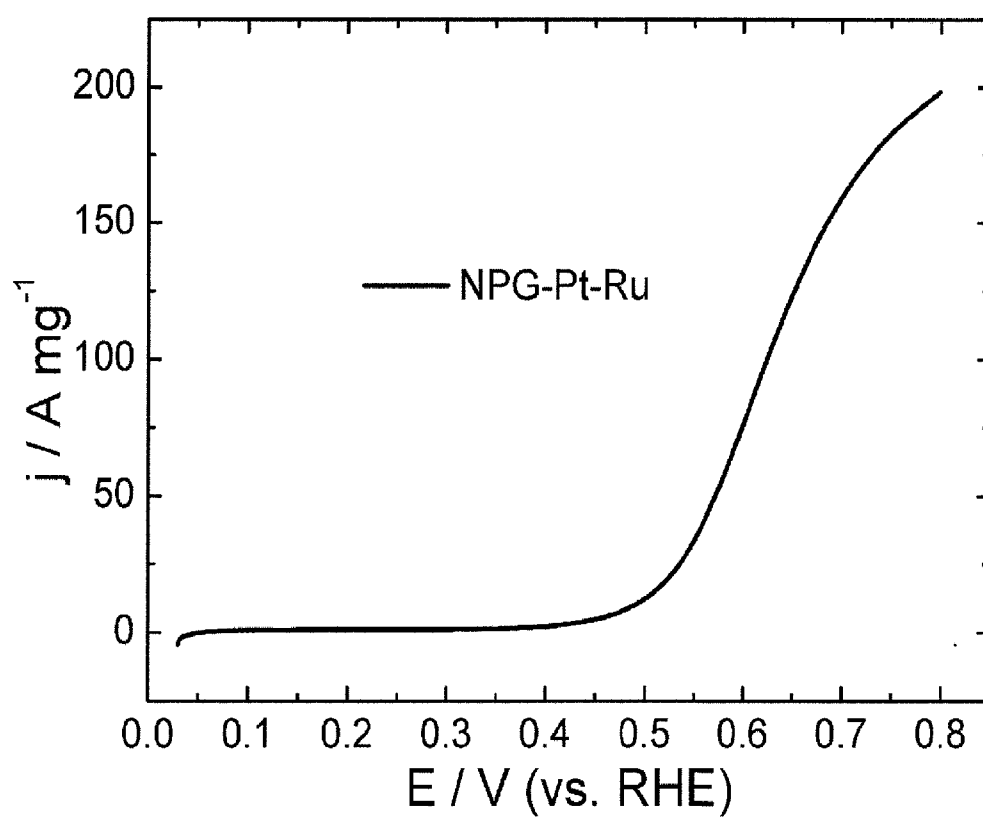


FIG.8

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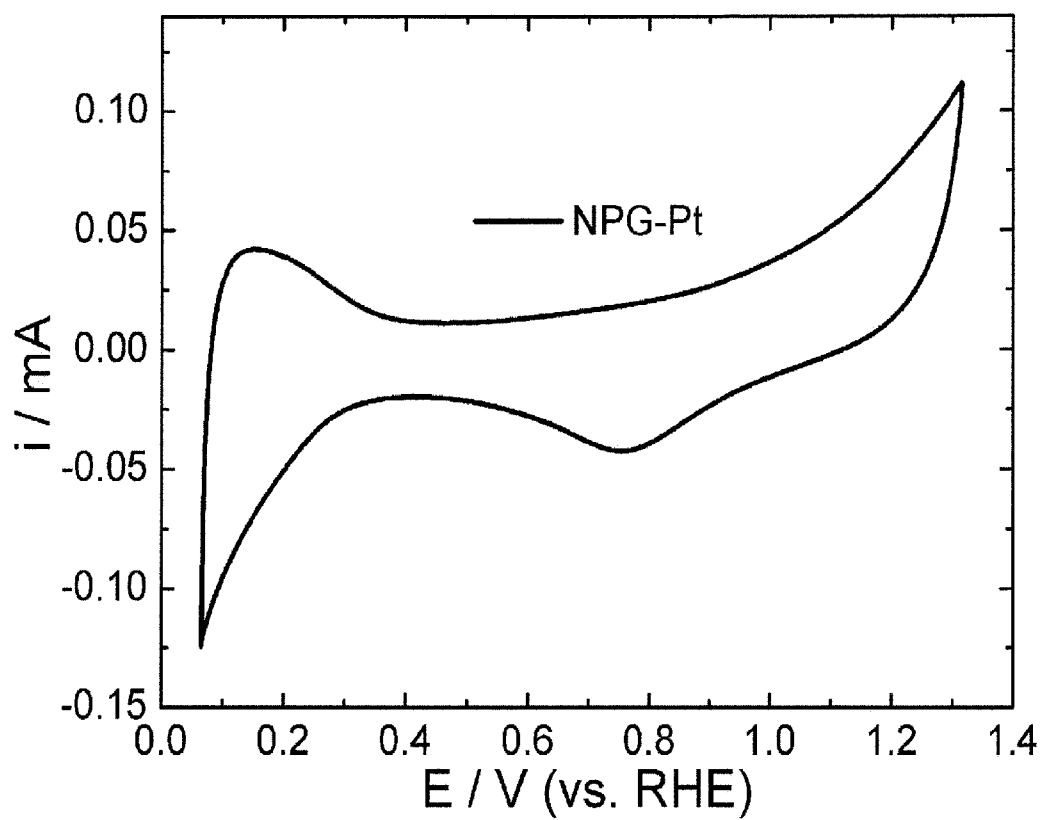


FIG.9

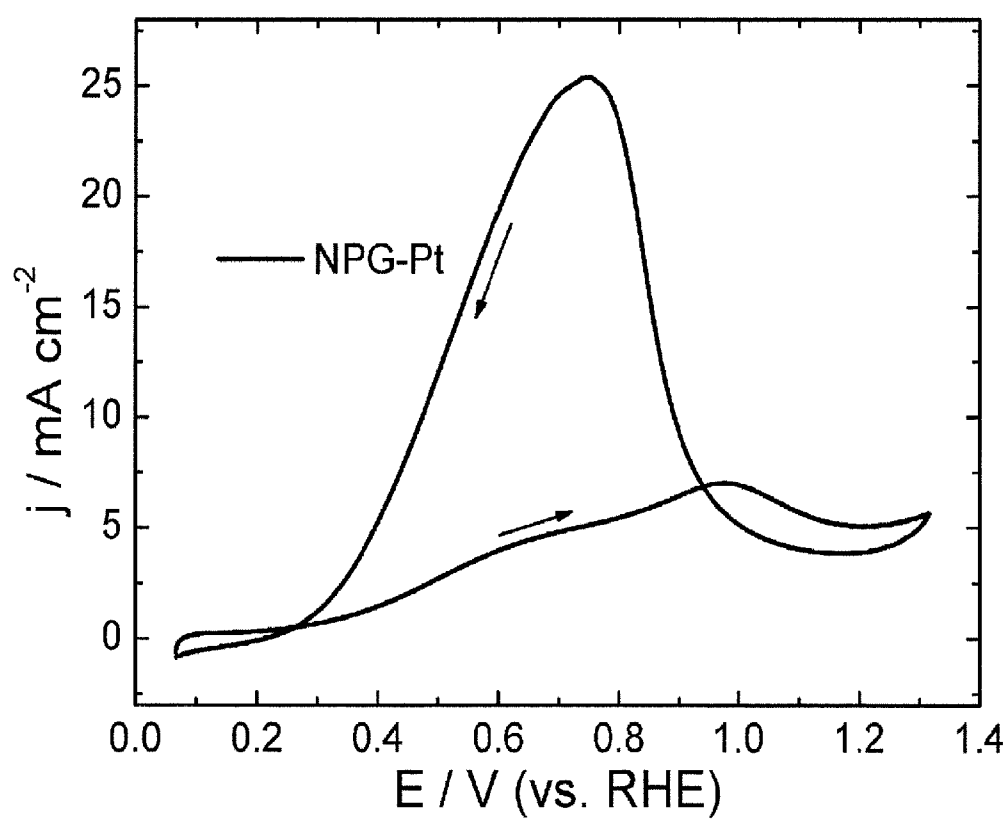


FIG.10

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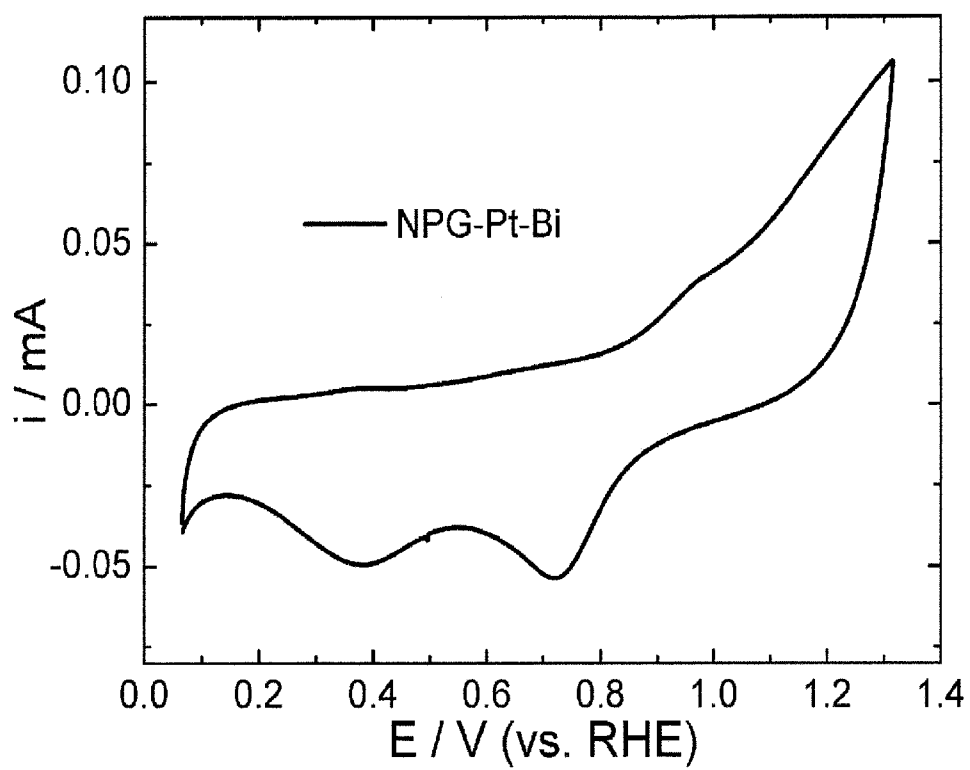


FIG.11

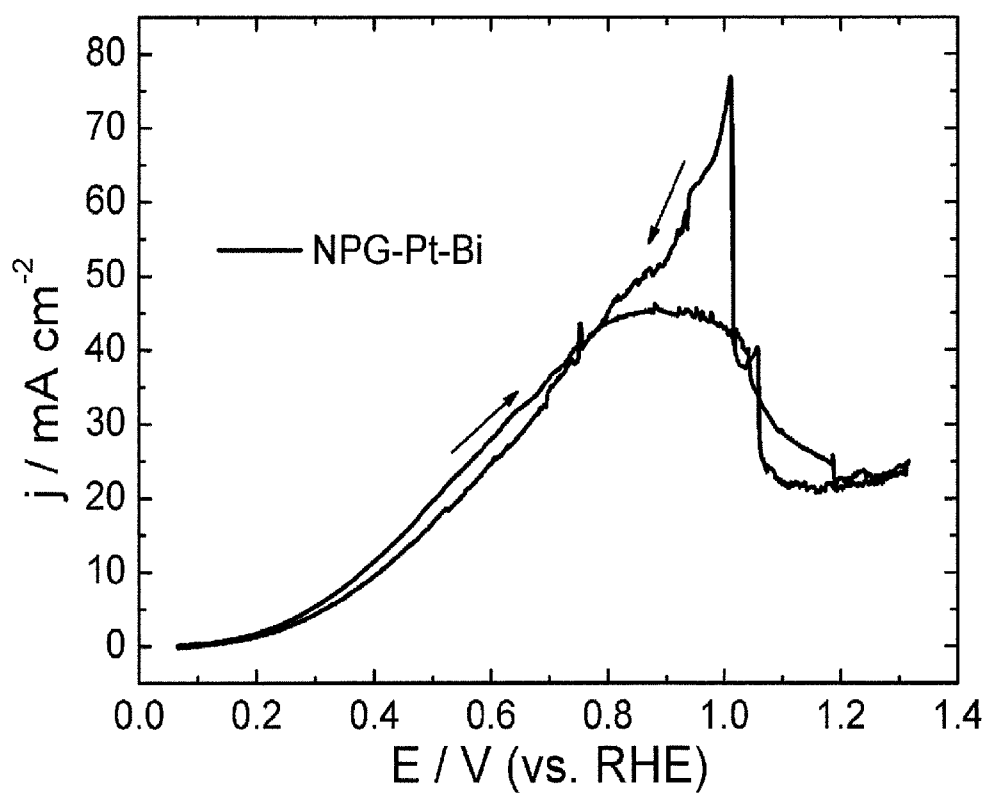


FIG.12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2011/022546

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	1-6 --- 7-17, 19-20
X --- Y	US 7,632,779 B1 (DING et al) 15 December 2009 (15.12.2009) entire document	18 --- 7-17, 19-20
Y	US 2010/0316931 A1 (WIELAND) 16 December 2010 (16.12.2010) entire document	12, 17, 19-20
A	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

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"O" document referring to an oral disclosure, use, exhibition or other means

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search

14 March 2011

Date of mailing of the international search report

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Name and mailing address of the ISA/US

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