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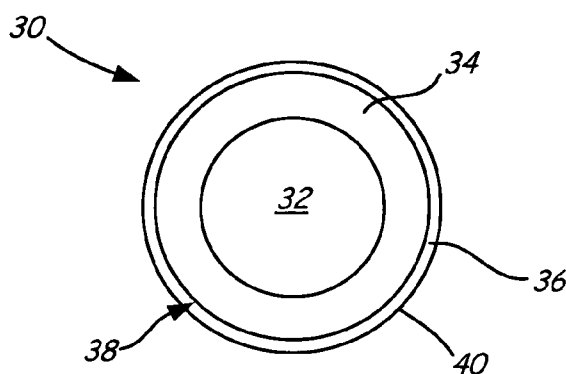


FIG. 2A

(57) Abstract: A catalytic structure comprises a metal oxide or metal phosphate core, a hexaboride coating and a catalyst. The hexaboride coating is deposited on the core. The catalyst is deposited on the hexaboride coating.

HEXABORIDE CONTAINING CATALYST STRUCTURE AND METHOD OF MAKING

BACKGROUND

5 Electrodes containing supported metal catalyst particles are used in electrochemical cells, such as fuel cells. For example, in a conventional hydrogen fuel cell, a supported platinum catalyst is used to oxidize hydrogen gas into protons and electrons at the anode of the fuel cell. At the cathode of the fuel cell, another supported platinum catalyst triggers an oxygen reduction reaction (ORR), leading to the formation of water.

10 The catalyst support is typically a conductive high surface area carbon. The catalyst support provides a surface over which the catalyst particles are dispersed and stabilized. The catalyst support is not just an inert substrate that supports the catalyst particles. Instead, because the catalyst particles are bonded to the catalyst support in some form, the catalyst support can greatly influence the catalytic activity and stability of the catalyst particles. It is well known that carbon supports have poor interactions with noble
15 metal catalyst particles. These poor catalyst-support interactions result in changes in electrode properties. More specifically, the poor catalyst-support interactions result in particle growth of catalyst particle sizes under dissolution/redeposition processes, which causes a loss in fuel cell performance. The poor interactions between the carbon catalyst
20 support and the catalyst particles can even result in irreversible loss of catalyst activity in the cathode.

Moreover, carbon catalyst supports in fuel cells are also susceptible to corrosion that results in carbon oxidation and, as a final stage, collapse of the carbon porous structure. Causes of corrosion include the presence of oxygen, water, and high electrode
25 potential, especially on the cathode side. Also, corrosion causes microstructural derogation and surface chemistry changes, which can result in an irreversible loss in catalyst performance and ultimately in the complete failure of the fuel cell. An improved catalyst support is therefore needed so that the performance of an electrochemical cell can be maintained.

SUMMARY

A catalytic structure comprises a metal oxide or metal phosphate core, a hexaboride coating and a catalyst. The hexaboride coating is deposited on the core. The catalyst is deposited on the hexaboride coating.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram of a fuel cell that uses the catalyst structures described herein.

FIG. 2A is a cross-sectional view of a catalyst structure having a catalyst thin film deposited on a hexaboride layer.

FIG. 2B is a cross-sectional view of a catalyst structure having catalyst particles dispersed on a hexaboride layer.

FIG. 3 is a graph illustrating the variation of the normalized electrochemical surface area (ESA) with the number of potential cycles for the catalyst structure of FIG. 2A and for a carbon core catalyst structure.

DETAILED DESCRIPTION

A catalyst structure is described herein which includes a metal oxide or metal phosphate core having hexaboride layer and a catalyst. The metal oxide or metal phosphate core provides increased corrosion resistance and catalyst-support interactions compared to a carbon core. The hexaboride layer facilitates spontaneous deposition of the catalyst. Thus, the catalyst structure has increased catalytic activity and stability when used in fuel cells and other electrochemical devices. In a specific example, a plurality of the catalyst structures forms the basis for electrochemical cell catalyst layers.

FIG. 1 is a schematic diagram of example fuel cell 10, which is designed for generating electrical energy and which includes anode gas diffusion layer (GDL) 12, anode catalyst layer 14, electrolyte 16, cathode gas diffusion layer (GDL) 18, and cathode catalyst layer 20. Anode GDL 12 faces anode flow field 22 and cathode GDL 18 faces cathode flow field 24. In one example, fuel cell 10 is a fuel cell using hydrogen as fuel and oxygen as oxidant. It is recognized that other types of fuels and oxidants may be used in fuel cell 10.

Anode GDL 12 receives hydrogen gas (H_2) by way of anode flow field 22. Catalyst layer 14, which may be a platinum catalyst, causes the hydrogen molecules to split into protons (H^+) and electrons (e^-). While electrolyte 16 allows the protons to pass through to cathode 18, the electrons travel through an external circuit 26, resulting in a production of electrical power. Air or pure oxygen (O_2) is supplied to cathode 18 through cathode flow

field 24. At cathode catalyst layer 20, oxygen molecules react with the protons from anode catalyst layer 14 to form water (H_2O), which then exits fuel cell 10, along with excess heat.

Catalyst particles dispersed and stabilized on catalyst support structures can form the basis of anode catalyst layer 14 and cathode catalyst layer 20. In one example, the catalyst particles are platinum. As described above, cathode catalyst layer 20 is used to increase the rate of the oxygen reduction reaction (ORR) ultimately resulting in the formation of water from protons, electrons and oxygen. Cathode catalyst layer 20 contains platinum as a catalyst. However, platinum suffers from dissolution in this environment. During potential cycling, platinum atoms tend to dissolve and redeposit. This dissolution/redeposition process results in catalyst particle growth that decreases the performance of the fuel cell.

In one example, fuel cell 10 is a polymer electrolyte membrane (PEM) fuel cell, in which case electrolyte 16 is a proton exchange membrane formed from a solid polymer. In another example, fuel cell 10 is a phosphoric acid fuel cell, and electrolyte 16 is liquid phosphoric acid, which is typically held within a ceramic (electrically insulating) matrix.

FIG. 2A is a cross-sectional view of catalyst structure 30 for use, for example, as a basis for anode catalyst layer 14 and cathode catalyst layer 20 in fuel cell 10. Catalyst structure 30 includes core 32, hexaboride layer 34 and catalyst 36. Hexaboride layer 34 is formed on at least a portion of core 32, and catalyst 36 is deposited on hexaboride layer 34.

Core 32 contains a stable metal oxide, a metal phosphate or a combination thereof. In one embodiment, core 32 contains titanium dioxide. In other examples, core 32 contains titanium phosphate, tantalum oxide or tantalum phosphate. Core 32 can be a nanoparticle. For example, core 32 can have a diameter between about 5 nm and about 50 nm.

In one example, core 32 is a high surface area core. Increasing the surface area of core 32 increases the catalytic activity of catalyst structure 30. Only the portion of catalyst 36 exposed to the external environment (i.e. the fuel cell environment) affects the catalytic activity of catalyst structure 30. By increasing the surface area of core 32, the surface area for deposition of catalyst 36 is increased, resulting in an increased number of exposed catalyst sites.

Hexaboride layer 34 is formed on at least a portion of the outer surface of core 32. In one example, hexaboride layer 34 completely covers the outer surface of core 32 so that hexaboride layer 34 encloses core 32. In another example, hexaboride layer 34 covers select portions of the outer surface of core 32.

5 Hexaboride layer 34 includes a metal hexaboride or mixture of metal hexaborides. In one example, hexaboride layer 34 includes lanthanum hexaboride, cerium hexaboride, calcium hexaboride and mixtures thereof. Hexaboride layer 34 includes compounds that have a low work function, such as below 5 eV. The low work function of hexaboride layer 34 allows catalyst 36 to spontaneously deposit, as described further below.
10 Additional, as described further below, the thickness of hexaboride layer 34 depends on the desired catalyst loading of catalyst structure 30.

Hexaboride layer 34 can be formed on core 32 by ball milling. Ball milling is a room-temperature deposition method. Alternatively, other methods, such as thermal synthesis, can be used to form hexaboride layer 34 on core 32.

15 Hexaboride layer 34 is a better electroconductive carrier than core 32 because hexaboride compounds are more electrically conductive than metal oxides and metal phosphates. Positioning hexaboride layer 34 between core 32 and catalyst 36 improves the electroconductivity and performance of catalyst structure 30.

Together hexaboride layer 34 and core 32 form catalyst support 38, on which
20 catalyst 36 is deposited. Catalyst 36 can be a noble metal catalyst such as gold, iridium, osmium, palladium, platinum, rhodium and ruthenium or alloys and mixtures thereof. Catalyst 36 can comprise catalyst nanoparticles have diameters between about 2 nanometers and about 100 nanometers. More specifically, catalyst 36 can comprise catalyst nanoparticles having diameters between about 2 nanometers and about 10 nanometers.

25 As shown in FIG. 2A, catalyst 36 can form catalyst layer 40 on catalyst support 38. Catalyst layer 40 is an atomically thin layer. In one example, catalyst layer 40 has a thickness of about 1 to 5 atomic layers. In another example, catalyst layer 40 has a thickness of about 1 atomic layer. Catalyst structure 30 has a low catalyst loading because catalyst layer 40 is a thin film. The low catalyst loading of catalyst structure 30 reduces the
30 cost of catalyst structures 30 and of fuel cell electrodes utilizing catalyst structures 30 because the majority of the cost associated with manufacturing electrodes for fuel cells is attributable to the high cost of the noble metal which makes up catalyst 36.

In one example, catalyst 36 is deposited by a substitution reaction between a catalyst precursor solution and hexaboride layer 34. Such a method includes forming a catalyst precursor solution, exposing support structure 38 to the catalyst precursor solution and spontaneously depositing catalyst 36 on support structure 38.

5 First, a catalyst precursor solution is formed by mixing a soluble catalyst precursor with a solvent. The soluble catalyst precursor is a precursor, such as a salt, of catalyst 36. For example, the soluble catalyst precursor can be a gold-precursor salt, an iridium-precursor salt, an osmium-precursor salt, a palladium-precursor salt, a platinum-precursor salt, a rhodium-precursor salt or a ruthenium-precursor salt. The solvent is a
10 solvent which dissolves the soluble catalyst precursor. The solvent can be an organic or aqueous medium. As explained below, the deposition conditions, such as the choice of solvent, affect catalyst 36.

Next, catalyst support 38 is exposed to the catalyst precursor solution. In one example, catalyst support 38 is exposed to the catalyst precursor solution by submerging it
15 in the catalyst precursor solution. In another example, the catalyst precursor solution is poured over catalyst support 38.

When catalyst support 38 is exposed to the catalyst precursor solution, catalyst 36 spontaneously deposits on hexaboride layer 34 because of the low work function of hexaboride layer 34. Work function is the minimum energy that must be given to an
20 electron in order to liberate it from the surface of a particular substance. The low work function of hexaboride compounds causes hexaboride layer 34 to readily give electrons to the catalyst precursor particles, leading to catalyst 36 depositing on top of the unreacted hexaboride compounds on catalyst support 38. For example, where hexaboride layer 34 is LaB_6 and catalyst 36 is platinum, the substitution reaction between hexaboride layer 34 and
25 the platinum catalyst precursor leads to the reduction of the catalyst precursor Pt ions to Pt atoms and oxidization of LaB_6 to La^{+3} and boron compounds B_x . The low work function of hexaboride layer 34 causes the catalyst 36 to deposit on catalyst support 38 by a substitution reaction in less than one minute. In one example, the substitution reaction can be a mole-to-mole substitution reaction so that one mole of hexaboride layer 34 is removed for every one
30 mole of catalyst layer 36 deposited.

Because catalyst 36 is deposited by a substitution reaction with hexaboride layer 34, in order to maintain hexaboride layer 34 between core 32 and catalyst 36 the thickness of hexaboride layer 34 deposited on core 32 must be thicker than the desired

thickness of hexaboride layer 34 in catalyst structure 30. The thickness of hexaboride layer 34 initially deposited on core 32 should be calculated based on the desired catalyst loading of catalyst structure 30, and should take into account the amount (or thickness) of hexaboride layer 34 that will be lost during the deposition of catalyst 36. When deposited, hexaboride layer 34 should be thick enough so that hexaboride layer 34 will be at least about 1 atomic layer thick after catalyst 36 is deposited on catalyst support 38. As explained above, hexaboride layer 34 is a better electroconductive carrier than core 32. Thus, having hexaboride layer 34 between core 32 and catalyst 36 improves the electroconductivity and performance of catalyst structure 30. In one example, hexaboride layer 34 is between about 1 and 10 atomic layers thick before catalyst layer 36 is deposited on support structure 38.

Catalyst structure 30 is more durable than previous catalyst supports having a carbon core. First, metal oxide or metal phosphate core 32 provides a catalyst structure with an improved corrosion resistance. Metal oxides and metal phosphates, such as titanium dioxide, are more corrosion resistant than carbon. In fuel cells and other electrochemical environments, carbon supports dramatically suffer from corrosion due to high potential excursion, especially during stop and start-up cycling. Corrosion results in carbon oxidation and, as a final stage, collapse of the carbon structure. The increased corrosion resistance of metal oxide or metal phosphate core 32 results in a more durable catalyst support.

Additionally, metal oxide or metal phosphate core 32 enhances the stability of catalyst 36. Carbon supports, such as carbon black, are very passive towards noble metal catalysts, such as platinum and platinum alloys. This results in significant particle growth of the platinum on the carbon black and a decreased catalytic activity. In comparison, metal oxides and metal phosphates are less passive towards noble metal catalysts, such as platinum and platinum alloys. Thus, core 32 results in catalyst structure 30 having a strong metal-support interaction (SMSI). Core 32 prevents or reduces the movement and agglomeration of the catalyst particles of catalyst layer 36. For example, when core 32 includes a metal oxide, the oxygen of the metal oxide perturbs the electronic environment of catalyst 36 by donating or attracting electrons. This leads to improvements in the catalyst activity of catalyst 36. When core 32 includes a metal phosphate, a similar increase in the catalyst activity of catalyst 36 is observed. The durability and stability of catalyst structure 30 can be further improved by the presence of other alloying elements, such as gold and iridium, in catalyst 36.

Although catalyst 36 has been described above as a thin film in catalyst structure 30, catalyst 36 can also be a plurality of distributed nanoparticles which do not form a thin film. As shown in catalyst structure 42 of FIG. 2B, a plurality of catalyst nanoparticles 44 can be dispersed on hexaboride layer 34. Similar to catalyst structure 30, catalyst structure 42 of FIG. 2B includes core 32 (which contains a metal oxide or a metal phosphate), hexaboride layer 34 and catalyst 36. Catalyst structure 42 functions the same as catalyst structure 30 and has the same benefits as described above. Additionally, catalyst structure 42 also has a low catalyst loading, which reduces the cost of catalyst structure 42.

Whether catalyst 36 forms catalyst layer 40 or a plurality of catalyst nanoparticles 44 dispersed on the surface of hexaboride layer 34 depends on the deposition conditions. For example, platinum catalyst particles deposited on a $\text{LaB}_6/\text{TiO}_2$ support structure 38 using an organic medium result in a platinum catalyst layer 40. In contrast, if the same work was performed using an aqueous solution, platinum catalyst nanoparticles 44 would disperse on the surface of catalyst support 38, not forming a thin film and resulting in a structure similar to catalyst structure 42 of FIG. 2B. The form of catalyst 36 does not significantly affect the catalyst structure. Both catalyst structure 30 and catalyst structure 42 having metal oxide or metal phosphate core 32 and hexaboride layer 34 have an improved stability and durability.

As illustrated in the following example, a catalyst structure comprising metal oxide or metal phosphate core 32, hexaboride layer 34 and catalyst 36 results in an improved catalyst structure compared to a carbon core catalyst structure. The following example is intended as an illustration only, since numerous modifications and variations within the scope of the present invention will be apparent to those skilled in the art.

EXAMPLE

Two catalyst structures were prepared and tested in an electrode cell with potential cycling. The first catalyst structure comprised a titanium oxide core, a lanthanum hexaboride layer on the titanium oxide core and a thin film of platinum catalyst on the lanthanum hexaboride layer ($\text{Pt}/\text{LaB}_6\text{-TiO}_2\text{-C}$). The second catalyst structure comprised a carbon core having platinum catalyst particles ($\text{Pt}/\text{KB TTK}$).

FIG. 3 shows the electrochemical surface area (ECA) of the platinum of both catalyst structures during potential cycle tests. As shown, the ECA for $\text{Pt}/\text{LaB}_6\text{-TiO}_2\text{-C}$ decreased more gradually than that for $\text{Pt}/\text{KB TTK}$. Further after 15,000 cycles, $\text{Pt}/\text{LaB}_6\text{-TiO}_2\text{-C}$ has a normalized ECA of about 65 while $\text{Pt}/\text{KB TTK}$ has a normalized ECA of

about 20. The higher ECA of Pt/LaB₆-TiO₂-C after 15,000 cycles and the more gradual decrease of ECA illustrates the enhanced catalytic activity and stability of the Pt/LaB₆-TiO₂-C catalyst structure.

5 Due to the similar properties, depositing a catalyst on any metal oxide or metal phosphate core with a hexaboride layer should result in a catalyst structure having a similarly increased catalytic activity and stability.

Although the present invention has been described with reference to preferred embodiments, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

10

CLAIMS:

1. A catalytic structure comprising:
a metal oxide or metal phosphate core;
a hexaboride coating on the core; and
5 a catalyst deposited on the hexaboride coating.
2. The catalytic structure of claim 1, wherein the catalyst is selected from the group consisting of gold, iridium, osmium, palladium, platinum, rhodium, ruthenium and alloys and mixtures thereof.
- 10 3. The catalytic structure of claim 1, wherein the catalyst is a thin film that is about 1 to 5 atomic layers thick.
4. The catalytic structure of claim 1, wherein the metal oxide or metal
15 phosphate core comprises titanium dioxide, titanium phosphate, tantalum oxide or tantalum phosphate.
5. The catalyst structure of claim 1, wherein the metal oxide or metal phosphate core comprises titanium dioxide.
- 20 6. The catalytic structure of claim 5, wherein the catalyst comprises platinum or a platinum alloy.
7. The catalytic structure of claim 6, wherein the hexaboride coating comprises
25 lanthanum hexaboride.
8. The catalytic structure of claim 1, wherein the hexaboride coating comprises lanthanum hexaboride, cerium hexaboride, calcium hexaboride or a mixture thereof.
- 30 9. The catalytic structure of claim 1, wherein the catalyst is a plurality of catalyst nanoparticles dispersed on the hexaboride coating.

10. The catalyst structure of claim 1, wherein the hexaboride coating comprises compounds having a work function below 5 eV.

11. A method of forming a catalytic structure, the method comprising:

5 forming a hexaboride coating on a metal oxide or metal phosphate core to create a catalyst support structure; and spontaneously depositing a catalyst on the catalyst support structure.

12. The method of claim 11, wherein the catalyst is selected from the group consisting of gold, iridium, osmium, palladium, platinum, rhodium, ruthenium and alloys and mixtures thereof.

13. The method of claim 11, wherein the step of forming the hexaboride coating on the metal oxide or metal phosphate core comprises ball milling.

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14. The method of claim 11, wherein the step of forming the hexaboride coating on the metal oxide or metal phosphate core comprises forming a hexaboride coating that is about 1 to 10 atomic layers thick.

20 15. The method of claim 11, wherein the step of spontaneously depositing the catalyst on the catalyst support structure comprises forming a catalyst precursor solution.

16. The method of claim 11, wherein the step of spontaneously depositing the catalyst on the catalyst support structure comprises depositing a catalyst layer that is about 1 to 5 atomic layers thick.

25

17. The method of claim 11, wherein the metal oxide or metal phosphate core comprises titanium dioxide, titanium phosphate, tantalum oxide or tantalum phosphate.

30 18. The method of claim 16, wherein the catalyst comprises platinum or a platinum alloy.

19. The method of claim 11, wherein the hexaboride coating comprises lanthanum hexaboride, cerium hexaboride, calcium hexaboride or a mixture thereof.

1/3

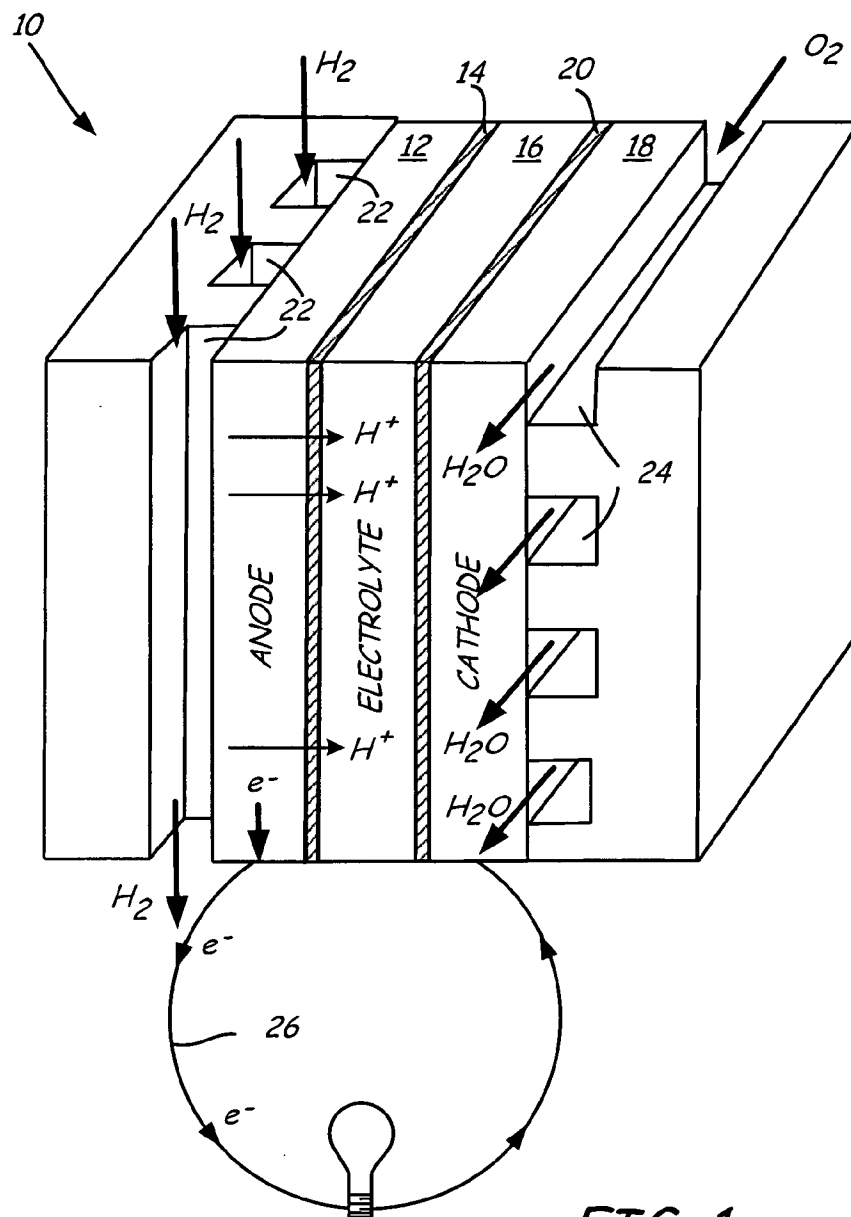


FIG. 1

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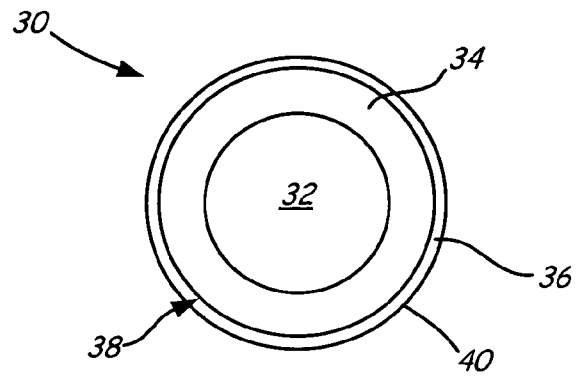


FIG. 2A

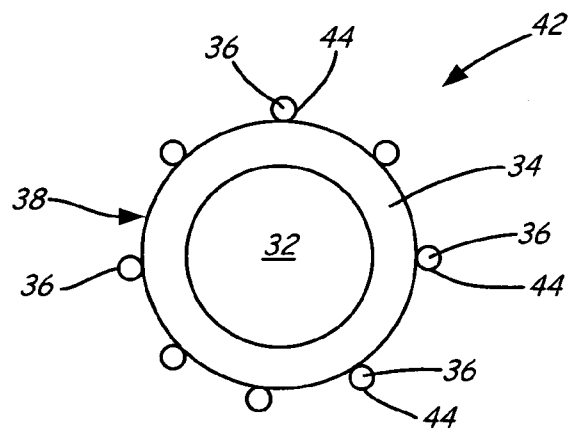


FIG. 2B

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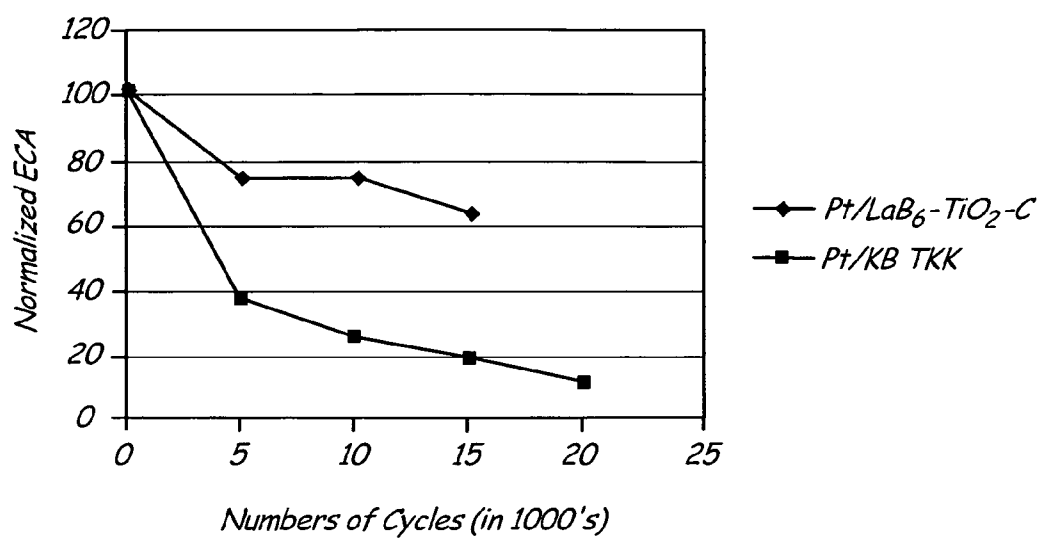


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2009/002987**A. CLASSIFICATION OF SUBJECT MATTER*****H01M 4/90(2006.01)i, H01M 4/88(2006.01)i, B01J 23/38(2006.01)i, B01J 21/06(2006.01)i, B01J 23/16(2006.01)i***

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: H01M 4/90, H01M 4/88, H01M 4/92, H01M 4/96, H01M 8/10, B01J 23/38, B01J 21/06, B01J 23/16, B05D 3/00

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

(Chinese Patents and application for patent)

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

eKOMPASS(KIPO internal) & keywords: fuel cell, catalyst, support, hexaboride, metal oxide, metal phosphate, spontaneous deposition, titanium dioxide, platinum

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	URIBE, FRANCISCO A. et al., Spontaneous Deposition of Noble Metal Films onto Hexaboride, Journal of the Electrochemical Society, 2007, Vol. 154, Iss. 11, Pages D623-D628 See figure 1, pages D624, D625, D628	1-3,8-16,19 4-7,17,18
Y	US 2006/0188775 A1 (MANCE, ANDREW M. et al.) 24 August 2006 See abstract, figure 2, claims 1-20	4-7,17,18
A	US 2007/0154639 A1 (MALINGER, KINGA A. et al.) 5 July 2007 See abstract, paragraphs 28, 33, 47	1-19
A	US 2007/0149399 A1 (KU, ANTHONY YU-CHUNG et al.) 28 June 2007 See abstract, figures 1-3, paragraphs 26, 29, 47	1-19
A	JP 2007-157646 A (CANON INC.) 21 June 2007 See abstract, paragraphs 19, 27, 29, claim 1	1-19



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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17 FEBRUARY 2010 (17.02.2010)

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Yang, Kyung Shik

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2006-188775 A1	24.08.2006	None	
US 2007-154639 A1	05.07.2007	None	
US 2007-149399 A1	28.06.2007	None	
JP 2007-157646 A	21.06.2007	None	