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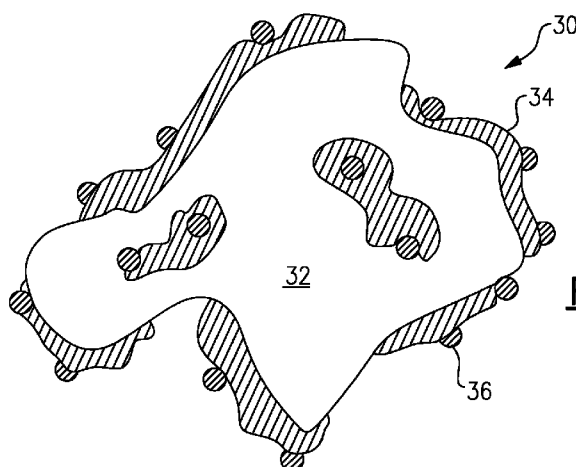
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(54) Title: FUEL CELL CATALYST SUPPORT WITH FLUORIDE-DOPED METAL OXIDES/PHOSPHATES AND METHOD OF MANUFACTURING SAME



**FIG. 2**

(57) Abstract: A fuel cell catalyst support includes a fluoride-doped metal oxide/phosphate support structure and a catalyst layer, supported on such fluoride-doped support structure. In one example, the support structure is a sub-stoichiometric titanium oxide and/or indium-tin oxide (ITO) partially coated or mixed with a fluoride-doped metal oxide or metal phosphate. In another example, the support structure is fluoride-doped and mixed with at least one of low surface carbon, boron-doped diamond, carbides, borides, and silicides.



## **FUEL CELL CATALYST SUPPORT WITH FLUORIDE-DOPED METAL OXIDES/PHOSPHATES AND METHOD OF MANUFACTURING SAME**

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### **TECHNICAL FIELD**

This disclosure relates to fuel cell catalyst supports and methods of manufacturing the same.

### **BACKGROUND**

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Cost and durability issues have made it difficult to commercialize fuel cells. Fuel cells utilize a catalyst that creates a chemical reaction between a fuel, such as hydrogen, and an oxidant, such as oxygen, typically from air. The catalyst is typically platinum loaded onto a support, which is usually a high surface area carbon.

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Some durability issues are attributable to the degradation of the support caused by corrosion. Electrochemical studies have indicated that the corrosion depends strongly on surface area and morphology structure of carbon. For example, it has been reported that carbon with high surface area, such as Ketjen Black, can corrode severely at potentials experienced during start and stop cycling of the fuel cell causing a dramatic loss in fuel cell performance. Accordingly, to overcome this particular durability issue, it may be desirable to use a support other than carbon that is more chemically and electrochemically stable.

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One possible alternative support for a catalyst is a metal oxide. Metal oxides can typically have a high surface area and good corrosion resistance, which are desirable for fuel cell applications. However, most of these high surface area metal oxides are not conductive, and are extremely hydrophilic. Hydrophilic supports can cause problems, such as electrode flooding, which leads to a significant drop in cell performance, especially at high current densities. As a result, metal oxide supports have not been applied in low temperature fuel cells.

What is therefore needed is a modified metal oxide that is suitable for use in a fuel cell environment.

### **SUMMARY**

5 A fuel cell catalyst support is disclosed that includes a fluoride-doped metal oxide/phosphate support structure and a catalyst layer, supported on such fluoride-doped metal oxide/phosphate. In one example, the metal oxide/phosphate support structure is a sub-stoichiometric titanium oxide and/or indium-tin oxide (ITO) partially coated or mixed with a fluoride-doped metal oxide/phosphate. In another example, the  
10 metal oxide/phosphate is fluoride-doped and mixed with at least one of low surface carbon, boron-doped diamond, carbides, borides and silicides.

These and other features of the disclosure can be best understood from the following specification and drawings, the following of which is a brief description.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 is a highly schematic view of an example fuel cell.

Figure 2 is a highly schematic view of an example metal oxide/phosphate catalyst support for the fuel cell shown in Figure 1.

Figure 3 illustrates a fluoride-doped metal oxide/phosphate having a boron-doped diamond conductive matrix.  
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Figure 4 illustrates a fluoride-doped metal oxide/phosphate having an indium-tin oxide (ITO) conductive matrix.

Figure 5 illustrates a fluoride-doped metal oxide/phosphate having a fluorinated carbon conductive matrix.

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### **DETAILED DESCRIPTION**

An example fuel cell 10 is schematically illustrated in Figure 1. The fuel cell 10 includes a cell 12 having an anode 14 and a cathode 18 arranged about a proton

exchange membrane 16. The anode 12 receives a fuel, such as hydrogen, from a fuel source 24. A pump 28 supplies an oxidant, such as air, from an oxidant source 26 to the cathode 18. In the example, the oxidant source 26 is a surrounding environment. The fuel and oxidant react in a controlled chemical process to produce electricity. The cell 12 and other cells 20 are arranged in a cell stack assembly 22, to provide enough electricity to power a load. The fuel cell 10 shown in Figure 1 is exemplary only and should not be interpreted as limiting the claims.

The anode 14 and cathode 18 typically include a catalyst arranged on a catalyst support. The catalyst support provides the support structure upon which a thin layer of catalyst is deposited. Typically, the catalyst is platinum and the catalyst support is carbon, such as ketjen black, carbon fibers or graphite.

This disclosure relates to a catalyst support 30 having a metal oxide and/or metal phosphate support structure 32, as shown in Figure 2. Example metal oxides include oxides of titanium (e.g.,  $\text{TiO}_2$  and  $\text{Ti}_4\text{O}_7$ ), oxides of zirconium ( $\text{ZrO}_2$ ), oxides of tungsten ( $\text{WO}_3$ ), oxides of tantalum ( $\text{Ta}_2\text{O}_5$ ), and oxides of niobium ( $\text{NbO}_2$ ,  $\text{Nb}_2\text{O}_5$ ). Other example metal oxides include oxides of yttrium, molybdenum, indium and/or tin (e.g., ITO). Example metal phosphates include  $\text{TaPO}_x$ ,  $\text{TiPI}_x$ , and  $\text{FePO}_x$ . Metal oxides/phosphates with a high surface area, are desirable so that the active catalyst layer can be correspondingly increased. Moreover, metal oxides/phosphates are highly corrosion resistant.

Metal oxides/phosphates are hydrophilic, which is undesirable in some applications due to electrode flooding, particularly in the low temperature fuel cells. Metal oxides are also non-conductive. So, catalyst supports typically must be somewhat conductive to ensure electrons at the catalyst layer pass through the support without experiencing an undesirable amount of resistance. As a result, a catalyst support must not be only more hydrophobic but also conductive to be suitable for use in a fuel cell. To this end, a fluoride-doped layer 34 is used with metal oxide/phosphate support structure 32 to support the catalyst layer 36.

While the catalyst support 30 is schematically shown as discrete, uniform layers, it should be understood that catalyst support 30 comprises a fluoride-doped layer 34 arranged between the metal oxide/phosphate support structure 32 and the catalyst layer 36. Example catalysts include noble metals, such as platinum, palladium, gold, ruthenium, rhodium, iridium, osmium, or alloys thereof. A secondary metal can also be used to reduce the amount of noble metal used. Example secondary metals include transition metals, such as cobalt, nickel, iron, copper, manganese, vanadium, titanium, zirconium and chromium.

The catalyst support 30 based on fluoride-doped metal oxides/phosphates includes at least the following examples:

**Example 1: Boron Doped Diamond (BDD) as conductive matrix**

In Figure 3, the fluoride-doped layer 34 is provided by fluoride doping the metal oxide/phosphate support structure 32. Fluoride doping provides good hydrophobicity that is desirable for water and reactants management in fuel cells. However, fluoride doping may not provide sufficient conductivity. As a result, it may be desirable to mix some conductive and stable materials, such as boron-doped diamond with the fluoride-doped metal oxide/phosphate support structure to provide both desirable hydrophobicity and conductivity. The conductive materials also include but are not limited to low surface area carbon (e.g., carbon fibers), carbides (including metal carbides), borides, and/or silicides.

**Example 2: Indium tin oxide as conductive matrix**

In Figure 4, metal oxides such as titanium oxide ( $\text{Ti}_4\text{O}_7$ ) and/or indium tin oxide (ITO) are used as conductive matrices and the fluoride-doped metal oxides/phosphates are used as the support to provide the hydrophobicity.

**Example 3: Fluorinated carbon as conductive matrix**

In Figure 5, fluoride-doped metal oxide/phosphates are used as catalyst supports, mixed with conductive fluorinated carbon. This system provides both conductivity and hydrophobicity.

- 5           Although an example embodiment has been disclosed, a worker of ordinary skill in this art would recognize that certain modifications would come within the scope of the claims. For that reason, the following claims should be studied to determine their true scope and content.

## CLAIMS

1. A fuel cell catalyst support comprising:  
a support structure including at least one of a metal oxide and a metal phosphate;  
5 a fluoride-doped layer on the support structure; and  
a catalyst layer supported on the fluoride-doped layer.
2. The fuel cell catalyst support according to claim 1, wherein the support structure includes oxides of at least one of titanium, zirconium, tungsten, tantalum, niobium,  
10 yttrium, molybdenum, indium and tin.
3. The fuel cell catalyst support according to claim 2, wherein the support structure includes phosphates of at least one of titanium, zirconium, tungsten, tantalum, niobium, yttrium, molybdenum, indium, and tin.  
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4. The fuel cell catalyst support according to claim 3, wherein the fluoride-doped layer is mixed with a conductive materials including at least one of a low surface area carbon, boron-doped diamond, carbides, borides, and silicides.
- 20 5. The fuel cell catalyst support according to claim 4, wherein the conductive material includes at least one of titanium oxide and ITO.
6. The fuel cell catalyst support according to claim 2, wherein the fluoride-doped layer includes a fluorinated carbon.  
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7. The fuel cell catalyst support according to claim 1, wherein the catalyst layer includes at least one noble metal.

8. The fuel cell catalyst support according to claim 7, wherein the noble metal includes at least one of platinum, palladium, gold, ruthenium, rhodium, iridium, osmium, or alloys thereof.

5 9. The fuel cell catalyst support according to claim 7, wherein the catalyst layer includes at least one transition metal.

10. The fuel cell catalyst support according to claim 9, wherein the transition metal includes at least one of cobalt, nickel, iron, copper, manganese, vanadium, titanium,  
10 zirconium and chromium.

11. A method of manufacturing a fuel cell catalyst support comprising the steps of:  
providing a support structure including at least one of a metal oxide and a metal  
phosphate;  
15 coating the support structure with a fluoride-doped layer; and  
depositing a catalyst layer on the fluoride-doped layer.

12. The method according to claim 11, wherein the support structure includes oxides  
of at least one of titanium, zirconium, tungsten, tantalum, niobium, yttrium,  
20 molybdenum, indium and tin.

13. The method according to claim 12, wherein the support structure includes  
phosphates of at least one of titanium, zirconium, tungsten, tantalum, niobium, yttrium,  
molybdenum, indium, and tin.

25 14. The method according to claim 13, wherein the catalyst layer is mixed with at  
least one of a low surface area carbon, boron-doped diamond, carbides, borides, and  
silicides.

15. The method according to claim 12, wherein the fluoride-doped layer includes a fluorinated carbon.

5 16. The method according to claim 15, wherein the support structure includes at least one of titanium oxide and ITO.

17. The method according to claim 11, wherein the catalyst layer includes at least one noble metal.

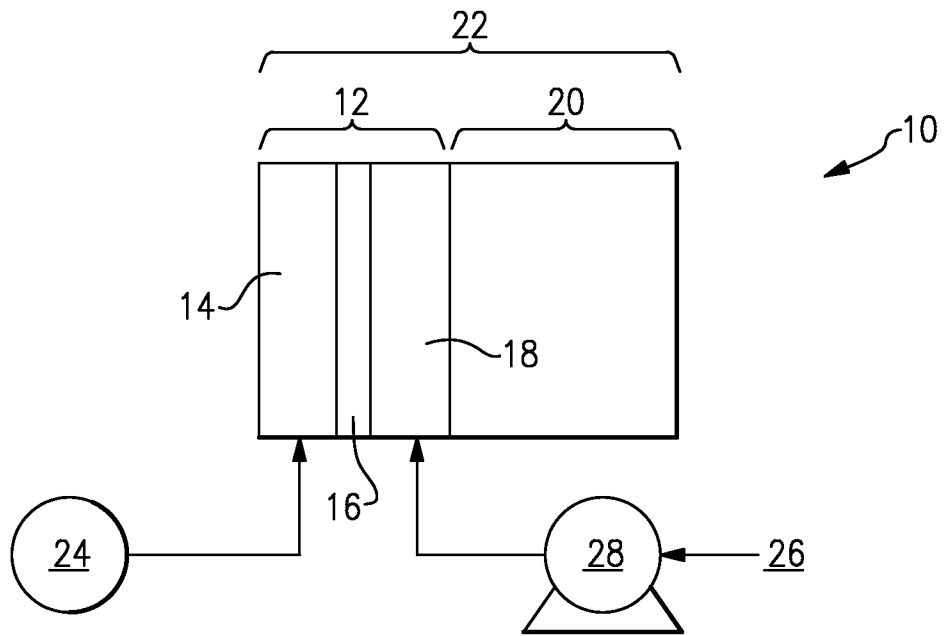
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18. The method according to claim 17, wherein the noble metal includes at least one of platinum, palladium, gold, ruthenium, rhodium, iridium, osmium, or alloys thereof.

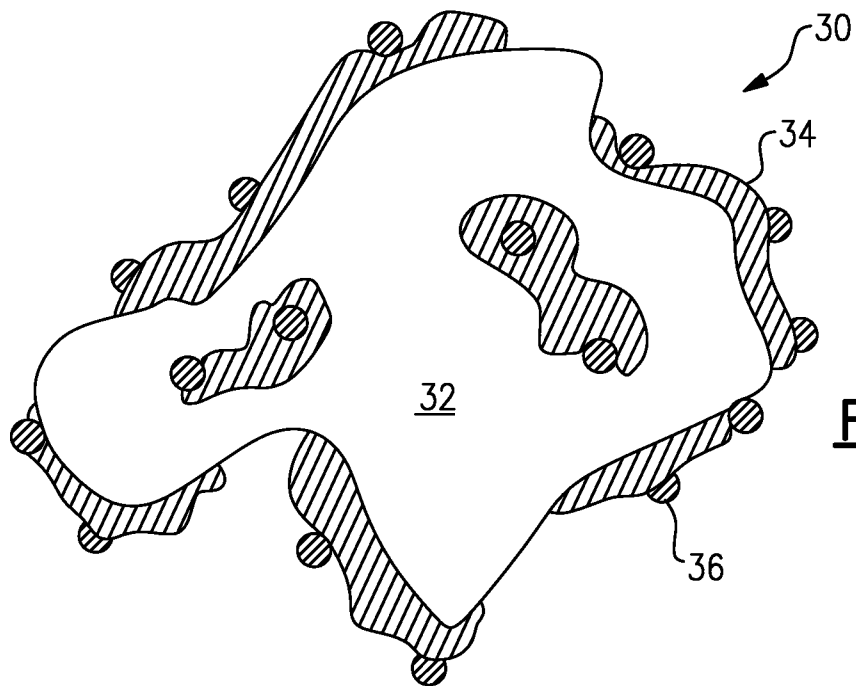
15 19. The method according to claim 17, wherein the catalyst layer includes at least one transition metal.

20. The method according to claim 19, wherein the transition metal includes at least one of cobalt, nickel, iron, copper, manganese, vanadium, titanium, zirconium and chromium.

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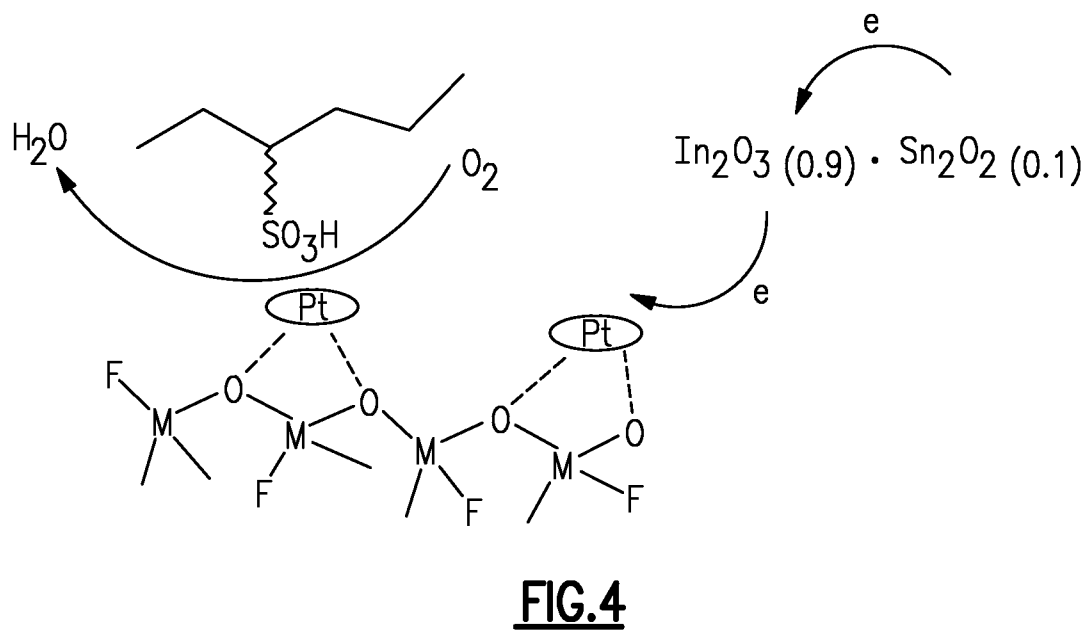
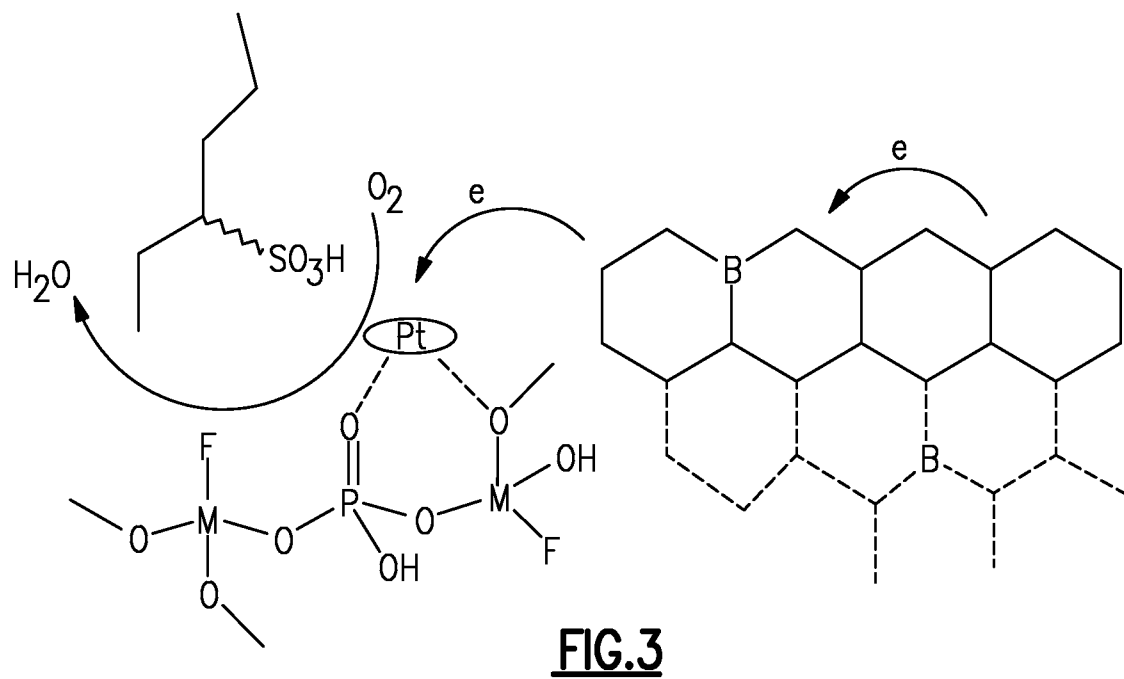


**FIG. 1**

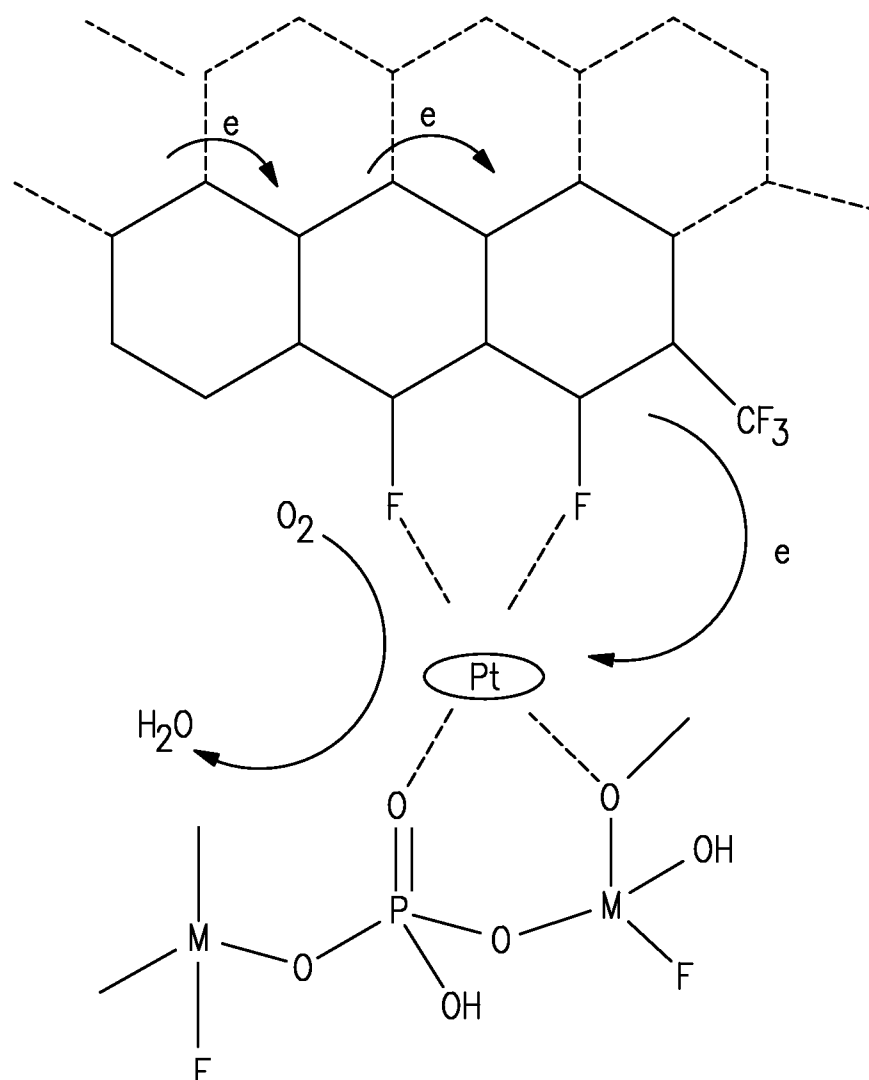


**FIG. 2**

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**FIG.5**

## INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/US2008/076577****A. CLASSIFICATION OF SUBJECT MATTER*****H01M 4/96(2006.01)i, H01M 4/86(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 8: H01M 4/96

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: IPC as above

Japanese Utility Models and Applications for Utility Models: IPC as above

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

e-KIPASS (KIPO internal) : "fuel cell", "catalyst", "metal oxide or metal phosphate", "fluoride dope\*", "hydrophobic", "conductive"

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                  | Relevant to claim No. |
|-----------|-----------------------------------------------------------------------------------------------------|-----------------------|
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| A         | US 5677074 A (SERPICO, Joseph M. et al) 14 Oct 1997<br>See Figs 1-2, and claims 1-12                | 1-20                  |
| A         | US 5783325 A (CABASSO, Israel, et al) 21 Jul 1998<br>See abstract, column 5-9, and Examples 1-7     | 1-20                  |
| A         | US 6811911 B1 (PELED, Emanuel, et al) 02 Nov 2004<br>See abstract and column 1-6                    | 1-20                  |
| A         | US 4643957 A (TAKEUCHI, Seizi, et al) 17 Feb 1987<br>See column 6-11 and claims 1-20                | 1-20                  |



Further documents are listed in the continuation of Box C.



See patent family annex.

\* 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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"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

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"&amp;" document member of the same patent family

Date of the actual completion of the international search

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Date of mailing of the international search report

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/US2008/076577**

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)                                                                                                                                                      | Publication<br>date                                                                                                                                    |
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