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Declaration under Rule 4.17:

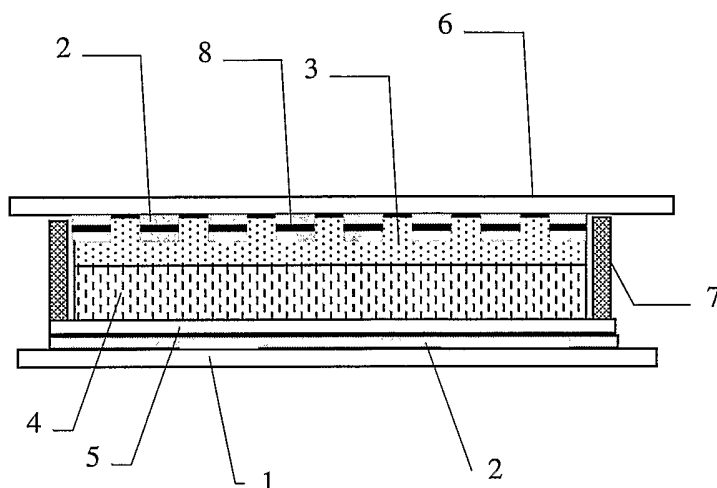
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For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: PHOTOELECTROCHEMICAL DEVICE



(57) Abstract: A photoelectrochemical (PEC) device comprising two substrates, wherein: at least one substrates is transparent and coated with Transparent Electronic Conductor (TEC); a working electrode comprising dye sensitised porous semiconductor is formed on one substrate; a counter electrode comprising catalytic layer is formed on another substrate; electrolyte is placed between said two substrates; metallic conductor are utilised to conduct electrical current within and from the device; a protective layer of non-metallic material, with sufficient electrical conductivity to enable viable electrical output from the PEC device, is used to protect the said metallic conductors from the electrolyte of the device.

Photoelectrochemical device

TECHNICAL FIELD

This invention relates to photovoltaic (PV) devices and more particularly, but not exclusively, to photoelectrochemical photovoltaic devices.

Further, this invention relates to methods of manufacturing such devices.

BACKGROUND TO THE INVENTION

A variety of photovoltaic devices are available for conversion of energy of electromagnetic radiation to electrical energy. These include a conventional solid-state devices (see M. Green *Third generation photovoltaics: concepts for high efficiency at low cost*, The Electrochemical Society Proceedings, Vol. 2001-10, p. 3-18) and more recently developed photoelectrochemical (PEC) devices

Examples of the PEC cells of the type concerned are disclosed in the following US patents:

4927721, Photoelectrochemical cell; Michael Graetzel and Paul Liska, 1990.

5525440, Method of manufacture of photo-electrochemical cell and a cell made by this method; Andreas Kay, Michael Graetzel and Brian O'Regan, 1996.

6,297,900, Electrophotochromic Smart Windows and Methods, G.E. Tulloch and I.L. Skryabin, 1997.

6,555,741, Methods to implement interconnects in multi-cell regenerative photovoltaic photoelectrochemical devices, J.A. Hopkins, G. Phani, I.L. Skryabin, 1999.

6,652,904, Methods to manufacture single cell and multi-cell regenerative photoelectrochemical devices, J.A. Hopkins, D. Vittorio, G. Phani, 1999.

Photoelectrochemical devices, as of the type disclosed in the above patents, are capable of being fabricated in a laminate arrangement between two large area substrates. One typical arrangement involves two glass substrates, each utilising an electrically conducting coating upon the internal surface of the substrate.

At least one of said first and second substrates is substantially transparent to visible light, as is the attached transparent electrically conducting (TEC) coating. PEC cells contain a working electrode, typically comprising a dye-sensitised, nanoporous semiconducting oxide (e.g. titanium dioxide known as titania) layer
5 attached to one conductive coating, and a counter electrode, typically comprising a redox electrocatalyst layer attached to the other conductive coating. An electrolyte containing a redox mediator is located between the photoanode and cathode, and the electrolyte is sealed from the environment.

10 Many photoelectrochemical devices would be advantaged by an increased size of the modules. However, the TEC coatings, which usually comprise a metal oxide(s), have high resistivity when compared with normal metal conductors, resulting in high resistive losses for large area photoelectrochemical cells, which affects the efficiency of the device especially in high illumination conditions.

15 Electrical resistance of substrates can be reduced by using metal plates, foils or metal mesh. Most of metals commonly used, however, are chemically reactive with the electrolyte of the photoelectrochemical cells. Corrosion of metallic components of PEC cells had been recognised as a major limitation to successful
20 commercialisation of PEC devices for many years.

In one arrangement the photoelectrochemical cells are connected in series, internally within a single module. Metallic conductors are used for such interconnection. Once again, choice of metallic conductors is limited to platinum and similar
25 metals, titanium and tungsten because of chemical interactions with the typical iodide containing electrolyte of a photoelectrochemical cell.

It is therefore an object of the present invention to provide a protective coating for low cost metallic conductors used in the photoelectrochemical cells that will solve
30 the combined problem of effective corrosion resistance without loss of effective performance while still being cost effective.

SUMMARY OF THE INVENTION

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In accomplishing the foregoing and related objectives, the invention provides for using layers of electrically conductive but chemically inert materials (e.g. diamond and electrically conducting nitrides and carbides) layers to conduct electrical current inside photoelectrochemical cell while protecting metallic components of the photoelectrochemical cell. It has been discovered that thin layers of these materials provide sufficient conductivity to electrically connect highly conductive metallic components, at the same time these materials are chemically inert towards electrolytes utilised in PEC. The electrical conductivity of the protecting layer can be modified by variation of composition or thickness so that the layer can be optimised for different applications (e.g. light conditions).

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The protective layers could be deposited using any known technology for their formation (e.g. arc deposition, sol-gel, sputtering, CVD, etc.). The layer is required to be sufficiently electrically conductive to enable viable electrical output while being chemically inert toward components of the photoelectrochemical cell.

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Considering conductive properties of such layers, the invention also provides for these layers being formed directly on substrate (glass, polymeric materials) without an intermediate metallic component, when requirement for electrical conductance are not high (e.g. – for low light conditions or small cell size).

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This invention is based on realisation that some materials such as titanium nitride form pinhole free strongly bound coatings that protect metallic conductors and, at the same time, provide electrical conductivity sufficient for successful operation of PEC device. Our experiments demonstrated that although unprotected 316 stainless steel substrate corrodes within several days of operation at room temperature, causing irreversible damage to electrolyte of the PEC device, a thin and dense layer of TiN coating deposited on the same substrate ensures many months of successful operations at 75 °C.

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Further analysis demonstrated that certain non-metallic materials satisfy requirements of corrosion protection and electrical conductivity by way of a several micron thick film.

These include: diamond and semimetallic, metallic (and multimetal) nitrides, carbides, oxides, borides, phosphides, silicides, antimonides, arsenides, tellurides
5 and combinations thereof (e.g oxynitrides, arsenide sulphides).

Still preferred materials for the purpose of this invention are: titanium nitride (TiN), zirconium nitride and boron carbide.

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Further preferred materials include silicides of niobium, molybdenum, tantalum, tungsten or vanadium.

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While this invention provides for a range of certain materials to be used for protection of the said metallic conductors, further description uses TiN as an example.

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In accordance with one aspect of the invention a TiN layer is deposited on metal foil or plate (e.g. stainless steel foil), thus protecting the foil from electrolyte of the cell.

The foil or plate serves as a substrate for either working or counter electrode of the photoelectrochemical cell.

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In accordance with another aspect of the invention a TiN layer is deposited on metallic mesh, used to conduct electrical current generated locally inside a cell to the external terminals. The mesh could be used in either or both working or/and counter electrodes of a photoelectrochemical cell.

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In accordance with a further aspect of the invention, a TiN layer is deposited on metallic conductor used to interconnect photoelectrochemical cells in a series connected module. In this case both the working electrode and the counter electrode are divided each into electrically isolated portions, and the said metallic

conductor connects at least one portion of the working electrode to a portion of the counter electrode

5 DESCRIPTION OF EXAMPLES

Having broadly portrayed the nature of the present invention, embodiments thereof will now be described by way of example and illustration only. In the following description, reference will be made to the accompanying drawings in which:

Figure 1 is an enlarged cross sectional view of a PEC device formed in accordance with one example of the invention.

Figure 2 is an enlarged cross sectional of a PEC device formed in accordance with another example of the invention

Figure 3a is an enlarged cross sectional of a PEC device formed in accordance with further example of the invention

Figure 3b is a diagrammatic representation of protected stainless steel mesh utilized in the previous example of the invention.

Referring to Figure 1 the working electrode substrate comprises Stainless Steel foil 1 protected by TiN coating 2. Working electrode 3 (dye sensitised TiO_2) formed on TiN coating (3 microns thick, filtered plasma deposition). The counter electrode 5 (thin dispersed Pt catalytic layer) of the device is formed on transparent electrically conductive substrate 6 (polymeric film coated by TEC). Electrolyte 4 is placed between the two electrodes. The device is sealed by silicone based sealant 7. This device is to be illuminated from the counter electrode side.

Referring to Figure 2A, a stainless steel foil 1 protected by TiN coating 2 supports counter electrode 5 of a PEC device. The working electrode is supported by a transparent electrically conductive substrate 6, to which a stainless steel mesh 8 coated by TiN 2 is attached. The said stainless steel mesh enhances electrical connection to a working electrode 3 (dye sensitised TiO_2). The device is sealed by silicone based sealant 7. This device is to be illuminated from the working electrode side.

Referring to Figure 2B, the stainless steel mesh 8 (50 μ aperture, 30 μ wire) is protected by TiN coating 2.

- 5 Referring to Figure 3, a PEC device is formed between two transparent substrates 6. Each substrate is coated by a transparent electronic conductor 9 (TEC, F-doped tin oxide). Isolation lines 10 in TEC created with aid of laser radiation divide each electrode into small portions. The working electrode substrate is coated by dye sensitised TiO₂ layer 3 and counter electrode substrate – by a
10 catalytic layer 5. 3 independent cells are formed by filling spaces between the electrode with an electrolyte 4. A conductor is used to connect the cells in series. The conductor comprises stainless steel core 11 protected by TiN coating 12.

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Claims:

1. A photoelectrochemical (PEC) device comprising two substrates, wherein
- at least one substrates is transparent and coated with Transparent Electronic Conductor (TEC);
 - a working electrode comprising dye sensitised porous semiconductor is formed on one substrate;
 - a counter electrode comprising catalytic layer is formed on another substrate;
 - electrolyte is placed between said two substrates;
 - metallic conductor are utilised to conduct electrical current within and from the device;
 - a protective layer of non-metallic material, with sufficient electrical conductivity to enable viable electrical output from the PEC device, is used to protect the said metallic conductors from the electrolyte of the device.
2. The PEC device according to claim 1, wherein the said metallic conductor is metallic plate or metallic foil.
3. The PEC device according to claim 2, wherein the said metallic plate or foil conducts electrical current from either the working or the counter electrode of the PEC device.
4. The PEC device according to claim 1, wherein the said metallic conductor is metallic mesh.
5. The PEC device according to claim 4, wherein the said metallic mesh is used to electrically connect either the working or counter electrode of the device.
6. The PEC device according to claim 1, wherein both the working electrode and the counter electrode are divided each into electrically isolated portions, and the said metallic conductor connects at least one portion of the working electrode to a portion of the counter electrode.
7. The PEC device according to claim 1, wherein the protective layer comprises diamond or semimetallic or metallic nitrides, carbides, oxides, borides, phosphides, sulphides, silicides, antimonides, arsenides, tellurides and combinations thereof.

8.The PEC device according to claim 8, wherein the said material is titanium nitride or zirconium nitride.

9.The PEC device according to claim 8, wherein the said carbide is boron carbide.

5 10. The PEC device according to claim 8, wherein the said silicide is silicide of niobium, molybdenum, tantalum, tungsten or vanadium.

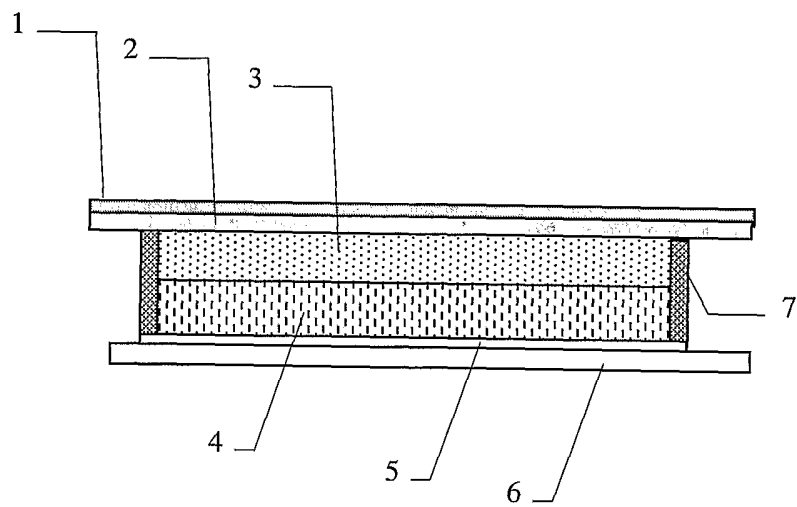
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**Figure 1.**

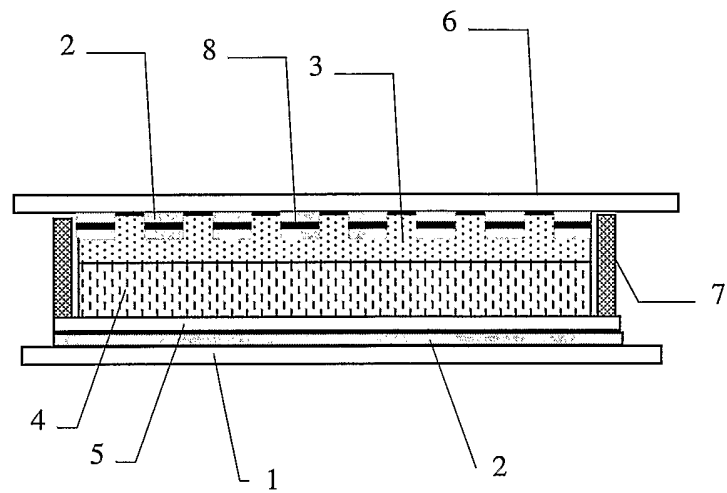


Figure 2A

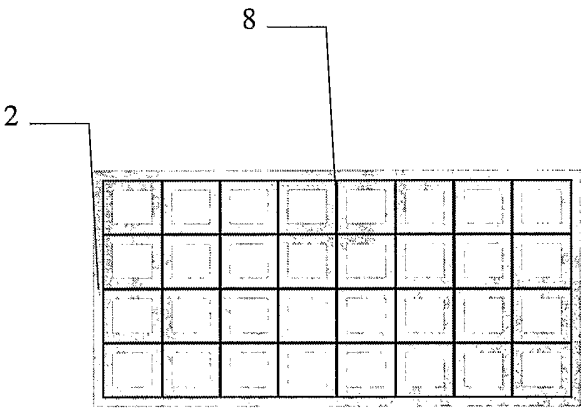


Figure 2B

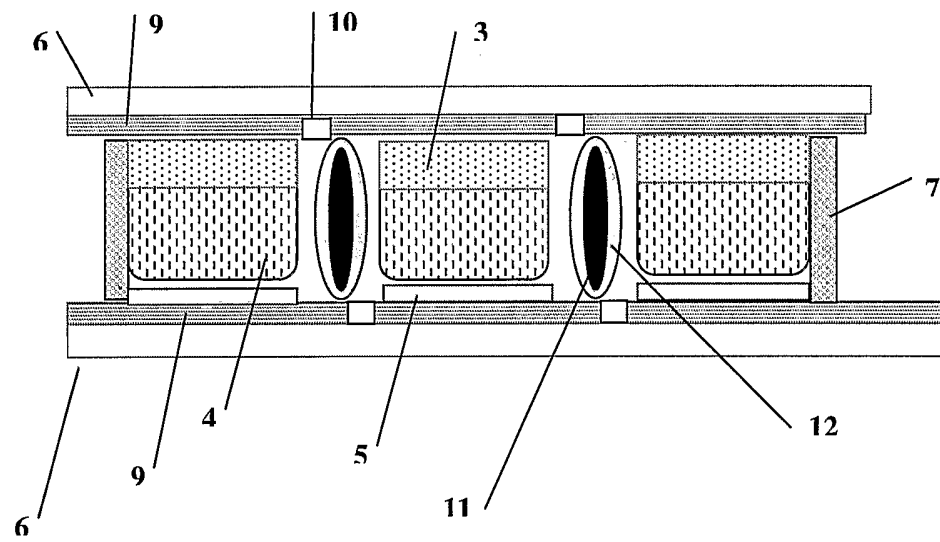
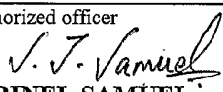


Figure 3.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2004/000590

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl. ⁷ : H01G 9/20, 9/26, 9/004; H01M 14/00, 6/36; H01L 31/05		
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)		
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) WPAT, USPTO, ESP@CE: Photoelectrochemical, RPEC, solar, conductor, wire		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2000/042674 A1 (LINDQUIST, Sten-Eric) 20 July 2000 Page 1, line 10 – page 4, line 20.	1
X	DE 19640616 A1 (PENTH BERND DR) 02 April 1998 Whole document.	1,7
Y	US 6,462,266 B1 (KURTH) 08 October 2002 Abstract, claim 1.	1
Y	WO 2000/062315 A1 (SUSTAINABLE TECHNOLOGIES AUSTRALIA LIMITED) 19 October 2000 Page 3, lines 11-19.	1
☒ 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 "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 28 July 2004		Date of mailing of the international search report - 4 AUG 2004
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer  SERINEL SAMUEL Telephone No : (02) 6283 2382

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2004/000590

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Patent Abstracts of Japan, JP, 2003-123860 (NEC CORPORATION) 25 April 2003 Abstract, fig. Note: For "Y" indications, each of the "Y" citation can be combined with any of the "X" citation	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2004/000590

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
WO	0042674	AU	24692/00	CA	2360350	EP	1151491
		SE	9900103	US	2002148721		
DE	19640616						
US	6462266	AU	22746/00	EP	1155424	WO	0048212
WO	2000062315	AU	35445/00	EP	1192627	US	6664623
JP	2003123860						
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.							
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