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(54) **PHOTOELECTROCHEMICAL DEVICE**

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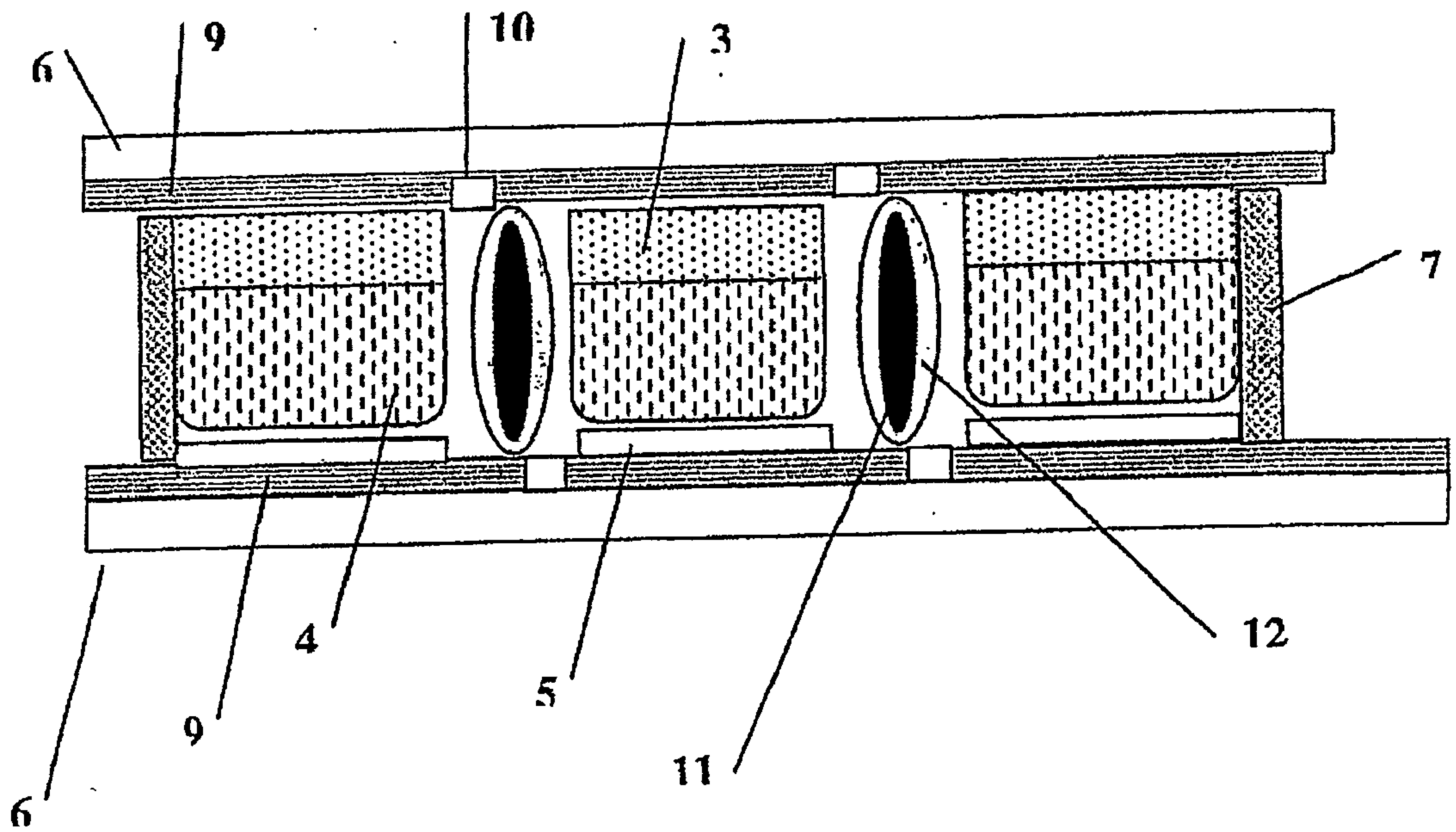
(57) **ABSTRACT**

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 the two substrates; metallic conductor are utilized 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 metallic conductors from the electrolyte of the device.



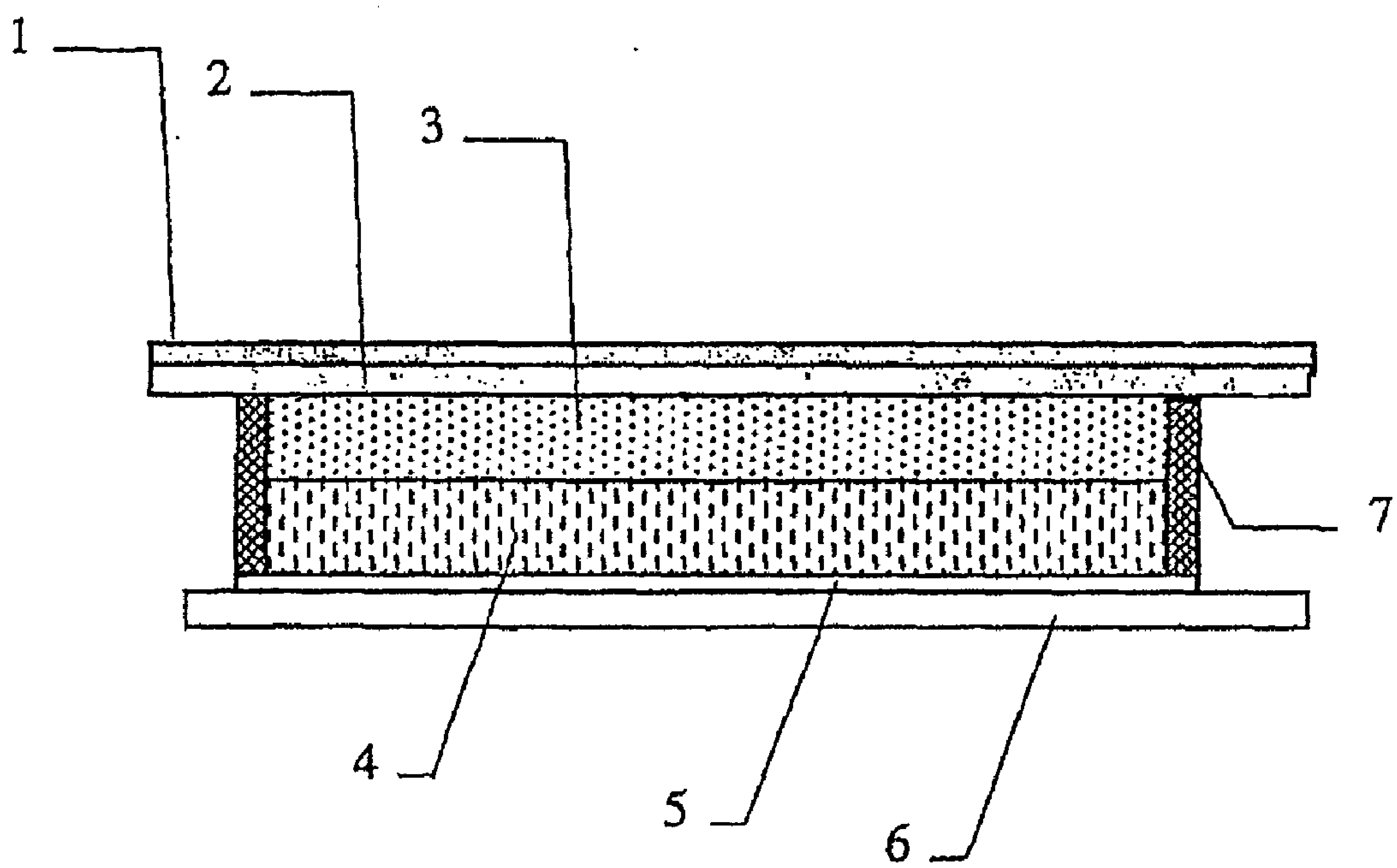


Figure 1.

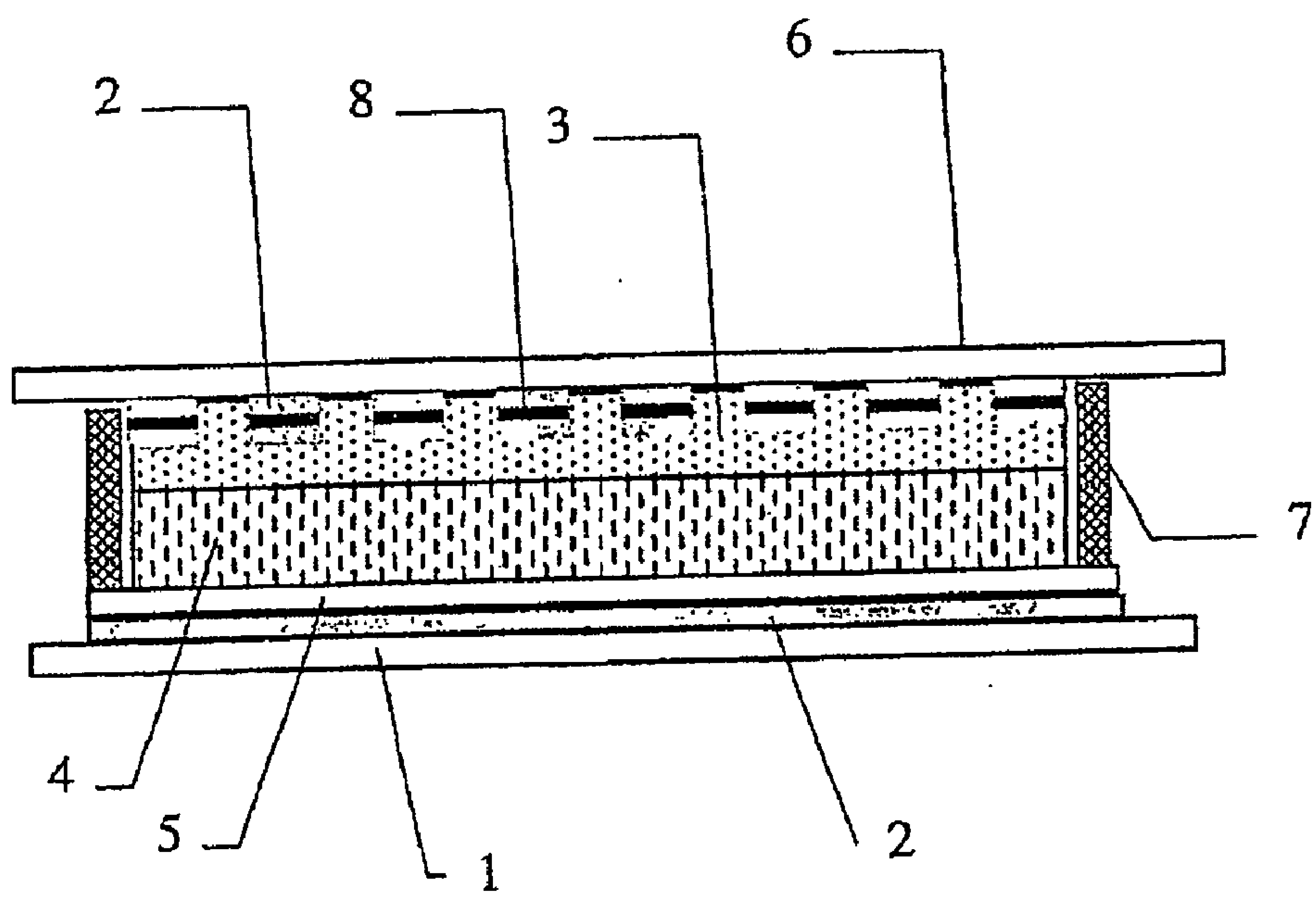


Figure 2A

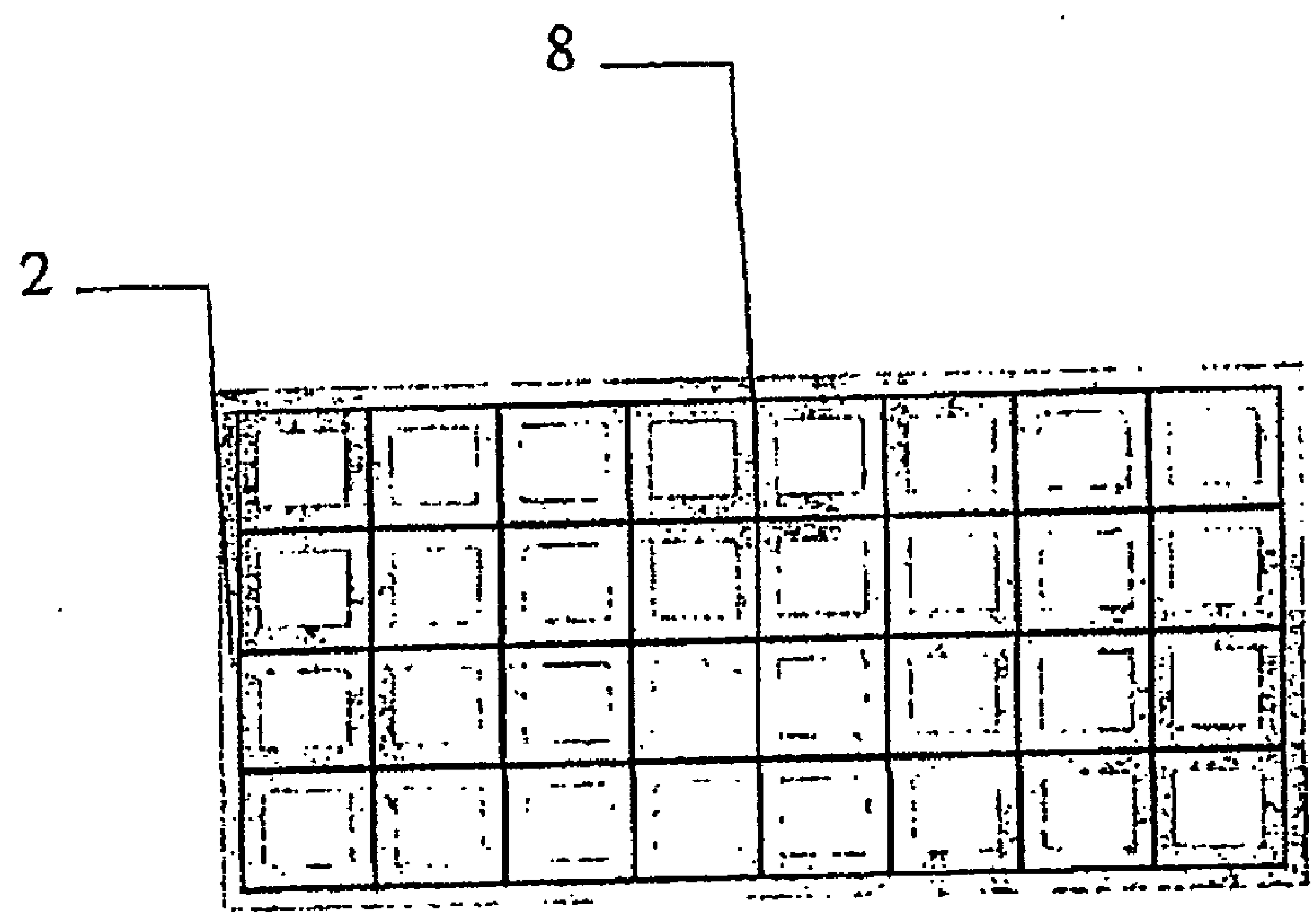


Figure 2B

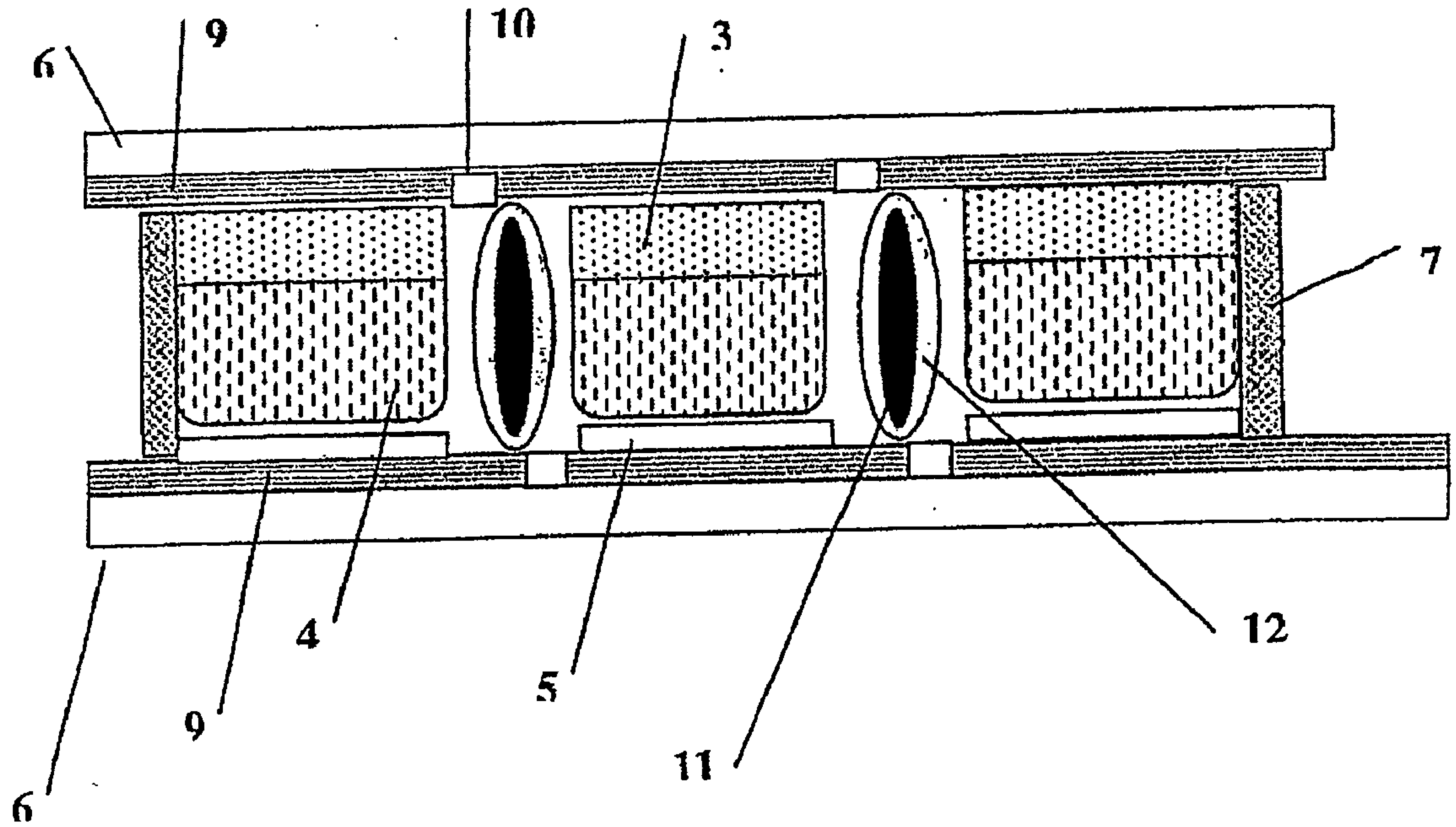


Figure 3.

PHOTOELECTROCHEMICAL DEVICE

[0001] This application is a national stage completion of PCT/AU2004/000590 filed May 5, 2004 which claims priority from Australian Application Serial No. 2003902117 filed May 5, 2003.

TECHNICAL FIELD

[0002] This invention relates to photovoltaic (PV) devices and more particularly, but not exclusively, to photoelectrochemical photovoltaic devices.

[0003] Further, this invention relates to methods of manufacturing such devices.

BACKGROUND TO THE INVENTION

[0004] 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

[0005] Examples of the PEC cells of the type concerned are disclosed in the following US patents:

[0006] U.S. Pat. No. 4,927,721, Photoelectrochemical cell; Michael Graetzel and Paul Liska, 1990.

[0007] U.S. Pat. No. 5,525,440, Method of manufacture of photo-electrochemical cell and a cell made by this method; Andreas Kay, Michael Graetzel and Brian O'Regan, 1996.

[0008] U.S. Pat. No. 6,297,900, Electrophotochromic Smart Windows and Methods, G. E. Tulloch and I. L. Skryabin, 1997.

[0009] U.S. Pat. No. 6,555,741, Methods to implement interconnects in multi-cell regenerative photovoltaic photoelectrochemical devices, J. A. Hopkins, G. Phani, I. L. Skryabin, 1999.

[0010] U.S. Pat. No. 6,652,904, Methods to manufacture single cell and multi-cell regenerative photoelectrochemical devices, J. A. Hopkins, D. Vittorio, G. Phani, 1999.

[0011] 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.

[0012] At least one of said first and second substrates is substantially transparent to visible light, as is the attached transparent electrically conducting (TEC) coating.

[0013] PEC cells contain a working electrode, typically comprising a dye-sensitised, nanoporous semiconducting oxide (e.g., titanium dioxide known as titania) layer 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.

[0014] 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.

[0015] 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 commercialisation of PEC devices for many years.

[0016] 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 metals, titanium and tungsten because of chemical interactions with the typical iodide containing electrolyte of a photoelectrochemical cell.

[0017] 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 the combined problem of effective corrosion resistance without loss of effective performance while still being cost effective.

SUMMARY OF THE INVENTION

[0018] In accomplishing theforegoing 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).

[0019] 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.

[0020] 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).

[0021] 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.

[0022] Further analysis demonstrated that certain non-metallic materials satisfy requirements of corrosion protection and electrical conductivity by way of a several micron thick film.

[0023] These include: diamond and semimetallic, metallic (and multimetal) nitrides, carbides, oxides, borides, phosphides, silicides, antimon ides, arsen ides, tellurides and combinations thereof (e.g oxynitrides, arsenide sulphides).

[0024] Still preferred materials for the purpose of this invention are: titanium nitride (TiN), zirconium nitride and boron carbide.

[0025] Further preferred materials include silicides of niobium, molybdenum, tantalum, tungsten or vanadium.

[0026] 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.

[0027] 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.

[0028] The foil or plate serves as a substrate for either working or counter electrode of the photoelectrochemical cell.

[0029] 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.

[0030] 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

DESCRIPTIONS OF EXAMPLES

[0031] 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:

[0032] **FIG. 1** is an enlarged cross sectional view of a PEC device formed in accordance with one example of the invention.

[0033] **FIG. 2A** is an enlarged cross sectional of a PEC device formed in accordance with another example of the invention.

[0034] **FIG. 2B** is a diagrammatic view of a stainless steel mesh protected by a TiN coating.

[0035] **FIG. 3** is an enlarged cross sectional of a PEC device formed in accordance with further example of the invention.

[0036] Referring to **FIG. 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).

[0037] 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.

[0038] Referring to **FIG. 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.

[0039] Referring to **FIG. 2B**, the stainless steel mesh **8** (**50**m aperture, **30** m wire) is protected by a TiN coating **2**.

[0040] Referring to **FIG. 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 TiO_2 layer **3** and counter electrode substrate—by a 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 a TiN coating **12**.

1.-**10**. (canceled)

11. A photoelectrochemical device comprising two substrates, wherein

at least one of the two substrates is transparent and coated with a transparent electronic conductor;

a working electrode comprising dye sensitised porous semiconductor is formed on one substrate;

a counter electrode comprising catalytic layer is formed on another substrate;

an electrolyte is placed between the two substrates;

metallic conductors 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 photoelectrochemical device, is used to protect the metallic conductors from the electrolyte of the device.

12. The photoelectrochemical device according to claim 11, wherein the metallic conductors comprise one of a metallic plate and a metallic foil.

13. The photoelectrochemical device according to claim 12, wherein the metallic plate or metallic foil conducts electrical current from either the working or the counter electrode of the photoelectrochemical device.

14. The photoelectrochemical device according to claim 11, wherein the metallic conductor is metallic mesh.

15. The photoelectrochemical device according to claim 14, wherein the metallic mesh is used to electrically connect either the working or counter electrode of the device.

16. The photoelectrochemical device according to claim 11, wherein both the working electrode and the counter electrode are divided each into electrically isolated portions, and the metallic conductor connects at least one portion of the working electrode to a portion of the counter electrode.

17. The photoelectrochemical device according to claim 11, wherein the protective layer is selected from the group consisting of diamond, semimetallic or metallic nitrides, carbides, oxides, borides, phosphides, sulphides, silicides, antimonides, arsenides, tellurides and combinations thereof.

18. The photoelectrochemical device according to claim 11, wherein the material is selected from the group consisting of titanium nitride and zirconium nitride.

19. The photoelectrochemical device according to claim 18, wherein the carbide is boron carbide.

20. The photoelectrochemical device according to claim 18, wherein the silicide is silicide selected from the group consisting of niobium, molybdenum, tantalum, tungsten or vanadium.

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