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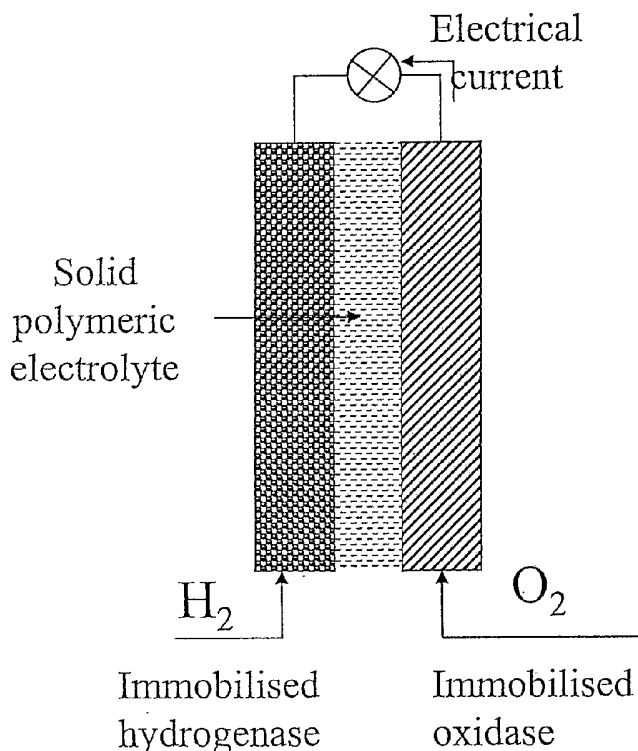
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(54) Title: HYDROGEN - OXYGEN FUEL CELL BASED ON IMMOBILIZED ENZYMES



(57) Abstract: The invention belongs to biotechnology and is applied for creation of electrochemical generators of electricity, in particular, fuel cells using molecular hydrogen as fuel and oxygen as oxidizer including that of air. The invention is based on application of enzymes capable of catalyzing the anodic and cathodic processes in place of platinum and other noble metals. Anode or hydrogen electrode contains the enzyme hydrogenase, in its composition, catalyzing activation and oxidation of molecular hydrogen. Cathode or oxygen electrode contains oxidase, in its composition, catalyzing activation and reduction of molecular oxygen directly from water. Cathode and anode are separated by the medium not conducting the electrons but providing the transfer of ions. Hydrogen-oxygen fuel cell, based on immobilized enzymes, features the fact that it contains (a) the hydrogen electrode made of carbonic matter where the enzyme hydrogenase is immobilized as hydrogen oxidation catalyst, (b) the oxygen electrode made of carbonic matter where the enzyme oxidase is immobilized as oxygen reduction catalyst and (c) the ionic conductor separating the two electrodes. The enzyme-based fuel cell has the following merits: (1) Enzymes are totally renewable catalysts; their production can provide a growing demand for fuel cells; (2) Costs of enzymes in their mass production are much lower than that of platinum; (3) Enzymic electrodes do not get poisoned

by admixtures of carbon oxide (CO) and hydrogen sulfide (H₂S) present in cheap fuels; and (4) Enzymes catalyze only their restricted reactions; the inevitable penetration of gasses into the opposite section of the fuel cell does not reduce its efficiency.



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

Hydrogen – Oxygen Fuel Cell Based On Immobilized Enzymes

BACKGROUND ON THE INVENTION

5 Field of the Invention

The present invention is related to biotechnology and is applicable to the creation of electrochemical electric generators, in particular, fuel cells using molecular hydrogen as fuel and oxygen as oxidizer, including that which is contained in air. The fuel cell is a converter of chemical energy of hydrogen oxidation into electricity. The invention is applicable to
10 vehicles, including motorcars, as well for domestic purposes for local energy source.

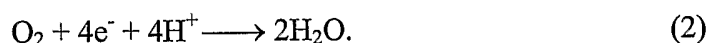
Discussion of Related Art

Fuel cells are chemical electric sources in which fuel is oxidized by an oxidizer. The fuel cell contains a negative electrode named anode and a positive electrode named
15 cathode. The electrodes are connected by an ionic conductor being a solution of electrolyte or ion-conducting polymer membrane. The interest in creation of fuel cells as electric current sources is explained by their high parameters as energy converters (efficiency 50-95%). The electrodes generate the in-between potential difference providing the electric current in the outer electric circuit.

20 For hydrogen–oxygen fuel cell, the electrochemical reaction running at the anode is expressed by the equation:



the cathodic process is, respectively, representable in the form of:



25 To-date, a few types of hydrogen–oxygen fuel cells are known to use both the liquid electrolyte (ion carrier) and the polymeric proton-conducting membrane. For instance, US Pat. No. 5,707,755 (1998) describes a fuel cell based on proton-conducting membrane as solid polymeric electrolyte (SPE). EP Pat. No. 127,414,612 (publication date 08.01.2003) uses phosphoric acid as ion-conducting medium. Application of the solid conductor NAFION
30 (sulfonated perfluorinehydrocarbon, EI DuPont de Nemours & Co.), as polymeric conductor in the fuel cell, was claimed in 1993 (US Pat. No. 5,272,017), (publication date: 21.12.1993).

The most elaborated devices at present are the fuel cells based on solid polymeric polyelectrolyte. According to the US Pat. No. 5,707,755, which can be considered as the nearest analogue, fuel cell of this type is the combination of membrane electrolyte and

electrodes, cathode and anode, on both sides of the separating polymer membrane. In this case, each electrode is tightly set at the polymeric proton-conducting membrane or partially placed into the membrane. Metallic platinum, applied on carbon materials of various structures, is used as catalyst both for anodic (reaction 1) and cathodic (reaction 2) processes.

5 This type pattern of membrane-electrode set increases the catalytic efficiency of cathode and anode processes, which appreciably reduces the expenditure of the noble metal. The optimum expenditure of platinum on cathode is 0.07 mg/cm^2 electrode, whereas this number on anode is three times less.

10 In all of the above patents, despite great discrepancies including constructive parameters, the general feature is the application of platinum and its alloys as catalysts if electrochemical ionization of hydrogen and oxygen are run by equations (1) and (2). This is due to unique features of platinum as catalyst of electrochemical reactions.

15 Multiple attempts were made to create electrodes for hydrogen-oxygen fuel cells based on metals other than platinum (see, for instance, the patents "Fuel Cell Anode Based on a Desired Catalytic Material" US Pat. No. 4,487,818 (1984-12-11) and "Fuel Cell Cathode" US Pat. No. 4,430,391 (1984-02-07)). However, they gave no notable positive results. The electrodes, based on these materials, demonstrated the redox potentials differing by 200-300 mV from the equilibrium values.

20 Thus, to-date, the best results are obtained upon application of metallic platinum, usually in a high-dispersion form, as catalysts both of anodic (reaction 1) and cathodic (reaction 2) processes. In addition, the drawbacks of platinum upon scaling-up are well known:

1) Platinum is a noble high-cost metal; its price in the world market keeps rising.

2) Platinum is a nonrenewable material; its regeneration from possible dispersed forms
25 is quite difficult (no more than 60%). Furthermore, all known reserves of platinum-containing ores, at current pace, may suffice but for 15-20 years of vehicle production.

3) The most notable drawback of platinum as catalyst is its high sensitivity to traces of carbon oxide (CO) and hydrogen sulfide (H_2S) contained in industrially produced hydrogen. Traces of CO and H_2S irreversibly inhibit (poison) platinum as catalyst of electrochemical
30 reactions.

The problem of irreversible inhibition (poisoning) of platinum by low concentrations of carbon oxide is particularly topical. To-date, the process, economically most grounded for industrial production of cheap hydrogen, is the complex scheme with reforming of methanol or hydrocarbon material. The reforming gas, theoretically containing 75% hydrogen and 25%

carbon dioxide, can be directly fed to the anode part of the fuel cell. In fact, however, the reforming gas contains nitrogen, oxygen and, what is more essential, a notably much greater quantity of carbon oxide. Depending on the method and degree of purification, CO content varies and can reach 2% v/v.

5 Platinum catalysts are highly sensitive to CO and actually become irreversibly inactivated at CO content higher than 10 ppm. There are known attempts to reduce the sensitivity of platinum catalysts to CO inhibitory action. So, the US Pat. No. 6,007,934 (1999-12-28) describes the procedure for preparation of the catalyst, affording one to increase its CO tolerance up to 100 ppm. However, the claimed tolerance increase was observed only for a
10 short time.

Even more important is the problem of poisoning platinum catalysts by H₂S, inevitably present in the content of so-called biogas, or microbiologically produced hydrogen. Hydrogen sulfide irreversibly interacts with platinum surface totally suppressing its catalytic activity. The operative time of electrodes in H₂S presence entirely depends on the rate of the
15 electro-catalytic poisoning. To provide the fuel cell performance for 1,000 hr, H₂S admixture in hydrogen should not be higher than 10 parts per billion (ppb). Evidently, that deep purification will sharply raise the price of the fuel.

The above parameters of platinum as catalyst of anodic and cathodic processes in fuel cells (high cost, limited resource, sensitivity to prevalent inhibiting admixtures) necessitate
20 the search for novel answers to the problem.

The present invention offers to apply enzymes as catalysts in fuel cells due to the following specific parameters of enzymatic catalysis:

- 1) Enzymes are high-activity biological catalysts. Calculations show that their catalytic activities are so high that their application can assist to reach high specific parameters of fuel
25 cells.
- 2) Enzymes are renewable catalysts that can be obtained in unlimited quantity, if necessary, from a renewable material. Enzymes are the catalysts having the properties (catalytic activity, stability, etc.) improvable by the methods of genetic engineering and protein design. There are conventional methods for industrial production of enzymes.

30 There are known systems demonstrating the potential applications of enzymes as catalysts in fuel cells. For instance, the company Powerzyme presented PCT patent application WO 02/086999 A1 (15.04.2002) for oxidation of C1 compounds, with the aid of dehydrogenases and electron carriers providing the coupling of enzymatic and electrochemical processes. A. Heller in US Pat. Application No. 2002/0025469 A1

(28.02.2002)) discusses biochemical fuel cells involving enzymes. This case demonstrated the possibility of applying the redox hydrogels and polymers for electron transfer between the electrode and the enzyme active site. The patent application describes the possibilities for applying various biological fluids and for creation of fuel cells implanted in plants, animals, and humans.

However, both of the above inventions of fuel cells, involving enzymes, do not consider the problem of creation of enzymatic hydrogen–oxygen fuel cell. In addition, both inventions envision the application of electron transfer mediators assisting the necessary electron exchange between the electrode and the enzyme active sites.

BREIF DESCRIPTION OF THE DRAWINGS

These and other features, aspects and advantages of the present invention will become better understood with regard to the following description, appended claims and accompanying drawings where:

Fig. 1 is a block diagram of the fuel cell in accordance with one embodiment of the present invention.

Fig. 2 is another illustration of the fuel cell in accordance with one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention aims to create a hydrogen–oxygen fuel cell and is based on a principally different approach. A ground of the present invention is to effect a direct electric contact between the electrode and the enzyme active site. The invention is based on the disclosed-by-authors capacity of enzymes to catalyze the electron transfer between the electron conductor (electrode) and substrate in electrolyte solution at a direct contact of the enzyme active site with the electron conductor.

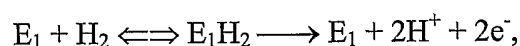
One basic feature of the invention is to use the enzymes capable of catalyzing both anodic (reaction 1) and cathodic (reaction 2) processes in place of platinum and other noble metals. Every enzyme is immobilized (adsorbed, chemically fixed) on the electron-conducting material, via its ingress into the electrode composition as an integral part of the electrode. Fig. 1 shows an embodiment of the present invention. Fuel cell 10 is comprised a hydrogen anode 12, an oxygen cathode 14, and an ionic conductor 16. Those skilled in the art would appreciate that the position of the anode and cathode as represented in the block diagram is of illustrative purposes only and can be re-arranged without departing from the scope and spirit

of the invention. Anode 12, or hydrogen electrode, contains in its composition a hydrogenase 18 activating and oxidizing molecular hydrogen. Cathode, 14 or oxygen electrode, contains in its composition an oxidase 20 effecting the activation and reduction of molecular oxygen directly from water. Cathode 14 and anode 12 are separated by an ionic conductor 16 that does not conduct electron, but ensuring the ion transfer. The ionic conductor (Nafion membrane, electrolyte solution) prevents the electron contact between anode and cathode and confines oxygen penetration into anodic (hydrogen) area of the fuel cell and the reverse.

Fig. 2 illustrates another schematic of the fuel cell explained in Fig. 1. The cell contains an immobilized hydrogenase (item 18 of Fig. 1) activating and oxidizing a hydrogen molecule, a immobilised oxidase (item 20 of Fig. 1) effecting the activation and reduction of a molecule of oxygen, and a solid polymeric electrolyte (item 16 of Fig. 1) separating the immobilised hydrogenase and the immobilised oxidase.

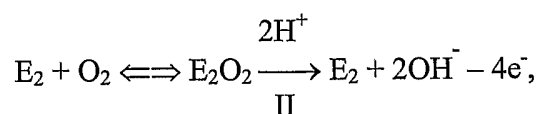
Two different enzymes, located on two spatially separated electrodes, generate electrochemical potentials equal or close in value to relevant equilibrium potentials (reactions 1 and 2), thus, providing the potential difference between the fuel cell electrodes.

On the anode, the enzyme E1 (hydrogenase) catalyzes the following reaction:



where E_1 is the enzyme active site; E_1H_2 is the enzyme-hydrogen molecule complex.

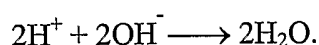
The irreversible stage is the electron transfer from the enzyme active site onto the electrode with release of two protons into the ion-conducting medium and with transfer of two electrons into the electron-conducting material.



where E_2 is the active site of the second enzyme; E_2O_2 is the enzyme complex with oxygen molecule.

Likewise, the second stage is the electron transfer from the electron conductor on the enzyme E_2 active site with reduction of oxygen molecules to hydroxyl ions.

In the ion-conducting medium, water is formed as the product of hydrogen oxidation by oxygen:



As for the merits of the enzyme-based fuel cell, one can accentuate the following:

1. Enzymes are entirely renewable catalysts; their production can provide the growing demand for fuel cells.
2. Enzyme costs notably fall up to 10 – 15 rubles (\$0.35-\$0.50 USD) per gram upon their mass production.
- 5 3. Carbon oxide (CO) and hydrogen sulfide (H₂S) admixtures, present in cheap fuels, do not poison the enzymic electrodes.
4. Enzymes catalyze only their restricted reactions; the inevitable penetration of gases into the opposite section of the fuel cell does not reduce the efficiency of energy conversion.

10 **Hydrogen fuel electrode based on immobilized enzymes**

Hydrogen fuel electrode can be designed by using the enzymes of the class of oxidoreductases that can activate and oxidize the molecular hydrogen. The enzymes of this type have got a trivial name, hydrogenases.

We demonstrated a possibility of applying hydrogenases from various sources for
15 creation of hydrogen fuel electrodes. For enzyme immobilization, various inert carbonic matters can be used as electric current-conducting carrier, such as graphite, carbon black, carbonic fabrics. To immobilize hydrogenases, the hydrophobic surface of the carrier can initially be: a) chemically or electrochemically hydrophilized, and b) modified by promoters.

Hydrogenases are immobilized by a) sorption from water solution and b) application
20 on carrier surface with the follow-up drying. For enzyme localization only on electrode surface, hydrogenase can be additionally stabilized by chemical crosslinking (for instance, application of glutaraldehyde) or by covering with water-insoluble polymer (for instance, Nafion).

The described procedures are demonstrated by the following parameters.

Example 1

Hydrophilize the carbonic fabric TBIII in concentrated sulfuric acid for 15 min, then wash it in phosphate buffer, pH 7.0, for 24 h. Place the fabric into the solution of hydrogenase isolated from the purple phototrophic sulfurbacterium *Thiocapsa roseopersicina*

- 5 (0,1 mg ml⁻¹) and allow it to stay for sorption at +4°C for 10-12 h. The resultant electrode in hydrogen-saturated water solution generates the open circuit voltage 3 – 10 mV relative to the equilibrium hydrogen potential. At overvoltage 200 mV, hydrogen oxidation current is 0.2 – 0.6 mA cm⁻².

Example 2

- 10 Electrochemically hydrophilize graphite rod in phosphate buffer, pH 7.0, via alternate polarization into anodic and cathodic sections (10 min.), setting the current density 30 mA cm⁻². Place the electrode into the solution of hydrogenase, isolated from sulfate-reducing bacterium *Desulfovibrio sp.* (1 mg ml⁻¹), and allow it to stay for sorption at +4°C for 12 h. The resultant electrode in hydrogen-saturated water solution generates the open circuit voltage 5 –
- 15 15 mV relative to the equilibrium hydrogen potential. At overvoltage 75 mV, hydrogen oxidation current is 0.1 - 0.2 mA cm⁻².

Example 3

- Apply the solution of promoter (polyviologen) in acetonitrile (0.1 mg ml⁻¹) on the carbonic fabric JIIII. Apply Water solution of hydrogenase, isolated from the purple
- 20 phototrophic sulfurbacterium *Th. roseopersicina* (0,1 mg ml⁻¹), on the fabric surface and dry at room temperature in air. The resultant electrode in hydrogen-saturated water solution generates the open circuit voltage 3 – 5 mV relative to the equilibrium hydrogen potential. At overvoltage 200 mV, hydrogen oxidation current is 0.5 – 1 mA cm⁻².

Example 4

- 25 Mix carbon black IIM-105 with Nafion solution in light alcohols up to Nafion content 15 –20% w/w. Apply the mixture on glassy-carbon rod and dry. Hydrophilize electrochemically the resultant electrode surface. Apply hydrogenase, isolated from the purple phototrophic sulfurbacterium *Th. roseopersicina* (0,05 mg ml⁻¹), on the electrode surface and dry at room temperature in air. In hydrogen-saturated water solution, the enzymic electrode
- 30 generates the open circuit voltage 3 – 5 mV relative to the equilibrium hydrogen potential. At overvoltage 200 mV, hydrogen oxidation current is 0.5 – 1 mA cm⁻².

Example 5

Prepare hydrogen enzymic electrode as shown in example 1 and stabilize it in glutaraldehyde vapors for 15 min. Electrochemical parameters of the electrode after treatment do not actually change.

5 Indisputable merits of hydrogen enzymic electrode compared to platinum electrode are its low sensitivity to carbon mono-oxide (CO) and hydrogen sulfide (sulfide anion) contained in hydrogen composition obtained by reforming and microbiologically, respectively.

Example 6

10 Prepare hydrogen enzymic electrode by examples 1 – 5, place it into the mixture of H₂ and CO. The electrochemical parameters of hydrogen enzymic electrode do not change at CO concentration up to 1%, which afforded the exploitation of the electrode in unpurified reforming gas. Furthermore, even after the hydrogen enzymic electrode has been exposed to 100% CO, the electrode totally recovers its activity as soon as it is placed back into hydrogen. For comparison, after the exposure of platinum fuel electrode to the mixture of H₂ and 0.1%
15 CO, the electrode was irreversibly inactivated by 99% for 10 min.

Example 7

Prepare hydrogen enzymic electrode by examples 1 – 5, place it into hydrogen-saturated solution, add sodium sulfide up to the final concentration 0.005 M. The electrochemical parameters of enzymic electrode do not change within the accuracy of
20 measurement error.

Oxygen enzymic electrode based on immobilized enzymes.

Oxygen electrode can be created by use of oxidase, catalyzing the reduction of molecular oxygen to water. Oxygen reduction to hydrogen peroxide is thermodynamically
25 inefficient: up to 50% energy is lost with hydrogen–oxygen fuel cell. As enzymes for oxygen electrode, one can use polyphenol oxidases (laccases), ascorbate oxidase, tyrosine oxidase and cytochrome c-oxidase.

The procedures for preparation of oxygen enzymic electrode are similar to those described above for hydrogen enzymic electrode. It is worthwhile, however, to demonstrate
30 them by the following examples.

Example 8

Hydrophilize the carbonic fabric ЖИИГ in concentrated sulfuric acid for 10 min. and wash it in phosphate buffer, pH 7.0, for 24 h. Place the fabric into the solution of laccase, isolated from the fungus *Coriolos hirsitus* (0.1 mg ml⁻¹), and sob it at +4°C for 12 h.

To stabilize the fabric surface, keep the electrode in glutaraldehyde vapors for 15 min. The resultant electrode, placed in oxygen, generates the open circuit voltage -30 – -50 mV relative to the equilibrium potential (oxygen/water); at overvoltage -200 mV, oxygen reduction current is 0.03 – 0.15 mA cm⁻².

5 Example 9

Suspend laccase, isolated from *Polyporus versicolor*, in isopropanol and mix it with Nafion solution. The final content of the enzyme and polyelectrolyte is to be 1 mg ml⁻¹ and 0.3%, respectively. Add the mixture to carbon black TIM-105 up to the polyelectrolyte content to be 20% relative to the carbonic matter and apply the resultant mixture on the glassy-carbon
10 plate. Dry the electrode in air. The resultant electrode, placed in oxygen, generates the open circuit voltage -30 – -50 mV relative to the equilibrium potential (oxygen/water); at overvoltage -200 mV, oxygen reduction current is 0.05 – 0.1 mA cm⁻².

Hydrogen–oxygen fuel cell

15 Example 10

Prepare hydrogen enzymic electrode as described above (examples 1-7). Prepare oxygen enzymic electrode according to examples 8-9. Place tightly the two electrodes to the proton-conducting Nafion membrane (specific resistance 20 Ω cm). Feed the gases to the electrodes separately: hydrogen to hydrogenase electrode, oxygen to oxidase electrode.
20 A stable potential difference, set in on the electrodes, is 1.15 – 1.18 V. In the equilibrium mode, the thermodynamic potential of the hydrogen–oxygen cell was established to be 1.23 V. Thus, the energy efficiency was 94% – 96% in this example. In absence of the enzymes on the above electron-conducting carriers, the potential difference was unstable and was within -0.3 – 0.5 V.

25 Example 11

Prepare hydrogen and oxygen enzymic electrodes as described in example 10. Place the two electrodes into the vessel with a general electrolyte (for instance, 0.05 M sodium acetate and 0.1 M sodium sulfate, pH 5.0), feed the gases separately: hydrogen to anode and oxygen to cathode. The potential difference, generated between the electrodes, is
30 1.16 – 1.19 V, which provides the efficiency of energy conversion 95% - 97%.

INDUSTRIAL APPLICABILITY

Hydrogen-oxygen enzymic fuel cell is applicable in the fields where platinum-based cells are employed. Examples include vehicles, local energy sources, electric generators using

hydrogen surplus, for instance, atomic electric stations. The merits: (a) they can be created by use of renewable catalysts and (b) they have no noble metals.

An essential merit of enzymic fuel cells is their weak sensitivity to carbon oxide and hydrogen sulfide. Insensitivity of hydrogenase electrode to H_2S makes it applicable upon
5 creation of the systems for production of electric energy from biological sources of hydrogen, for instance, upon conversion of organic wastes.

CLAIMS

We claim:

1. A hydrogen–oxygen fuel cell, based on immobilized enzymes, comprising:
5 (a) a hydrogen electrode made of carbonic matter, where enzyme hydrogenase is immobilized as hydrogen oxidation catalyst;

(b) an oxygen electrode made of carbonic matter, where enzyme oxidase is immobilized as oxygen reduction catalyst; and

(c) an ionic conductor separating the two electrodes.

10 2. The hydrogen–oxygen fuel cell of claim 1, wherein the carbonic matter is hydrophilized chemically, electrochemically or modified by promoters.

15 3. The hydrogen–oxygen fuel cell of claim 1, wherein the enzymes are immobilized by sorption from water solution or by its application on the carbonic matter surface with the follow-up drying.

20 4. The hydrogen–oxygen fuel cell of claim 1, wherein the immobilized enzymes are stabilized by chemical crosslinking or by coating with water-insoluble polymer.

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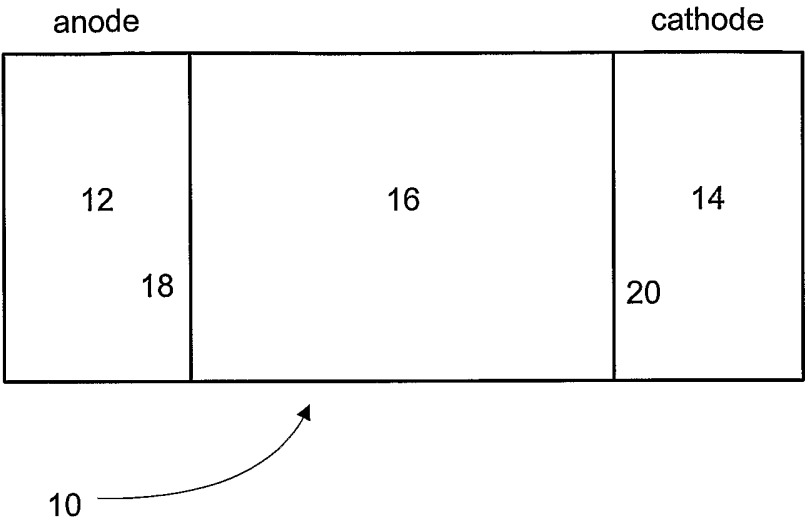


FIGURE 1

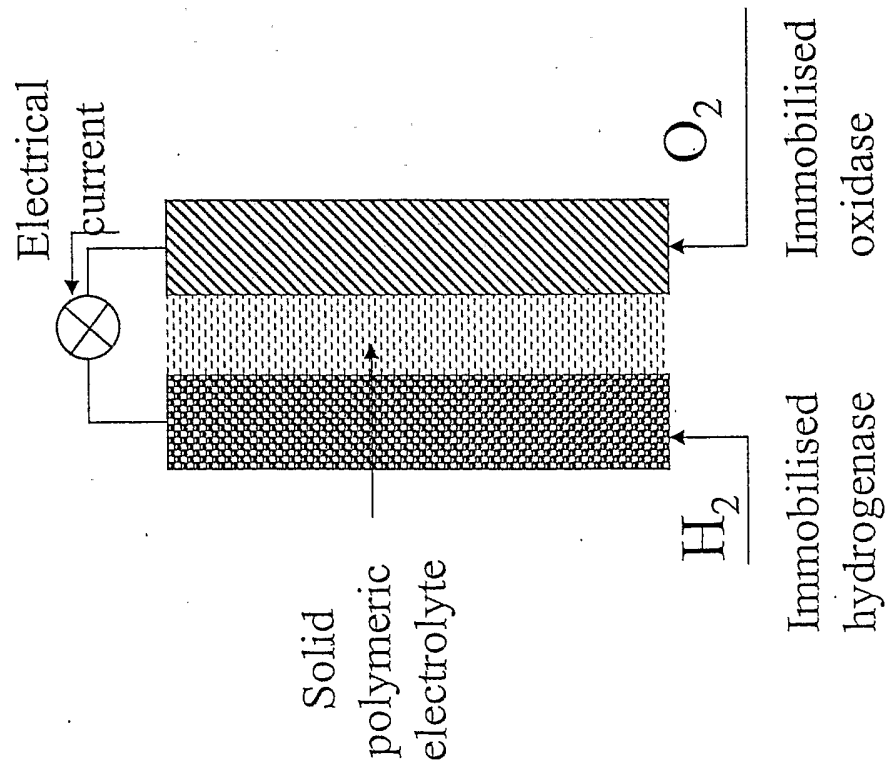


Figure 2