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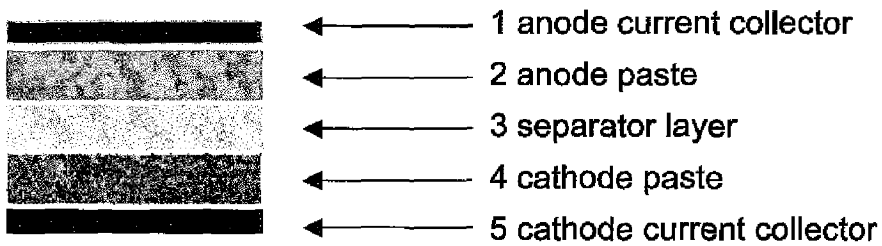
(54) Title: ENZYMATICALLY CATALYZED HYBRID ELECTROCHEMICAL CELL



(57) Abstract: The present invention relates to an electrochmical cell using enzyme catalyst comprising: a metal-based anode comprising an anode current collector and an anode paste; a cathode comprising a cathode current collector and a cathode paste or ink including enzyme catalyst; and a separator layer between said anode and cathode.

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ENZYMATICALLY CATALYZED HYBRID ELECTROCHEMICAL CELL

FIELD OF THE INVENTION

The present invention generally relates to the field of electrochemical cells providing electrical power. More particularly, the present invention relates to a hybrid structure where conventional battery technology is joined with fuel cell technology using enzyme as catalyst.

BACKGROUND OF THE INVENTION

Biological fuel cell is an electrochemical device converting energy from chemical reactions to electrical energy by means of the catalytic activity of living cells and/or their enzymes. The operating principle is similar to that of chemical fuel cells. The main difference is that the catalyst in a biological fuel cell is enzyme and not noble metal, such as platinum.

There is a lot of literature available which relates to fuel cells utilizing enzyme catalysts for improving the anodic and cathodic kinetics. More specifically, there are fuel cells which use enzyme catalysts either in the cathode compartment or in the anode compartment or both. US Patent Application Publication No. 2005/0164073 A1), e.g., describes a fuel cell using at least in the cathode compartment and optionally in the anode compartment oxidoreductase enzymes. US Patent Application Publication Nos. 2002/0164073 A1 and 2005/0095466 A1 describe fuel cells where both anode and cathode reactions are enzyme-catalyzed. Further, US Application Publication No. 2005/0158617 A1 and EP Patent application No. 1376729 A2 describe fuel cells where anode reactions are enzyme-catalyzed, and cathode reactions are catalyzed enzymatically or chemically.

There is interest for providing an electrochemical cell that is mechanically flexible, small in size and can be disposed with normal household waste. The output demand for these electrochemical cells is not high, only up to 1-2 mW, but enough to provide power to simple electronic circuits in disposable mass products, like active or semi-active RFID tags. Biological fuel cells offer a notable alternative to conventional battery technology in these applications. All the solutions described in the patent applications mentioned above are biological fuel cell systems in which a fuel, such as carbohydrates like glucose, alcohols etc., employed in the anode compartment is degraded to free electrons, protons and other reaction products. These known fuel cells do not possess, however, all said features of interest thus having different application area from that of the flexible and disposable ones. One of the main disadvantages associated with the known fuel cells using enzymes both as anode and cathode catalysts is the fact that they have a relatively low open-circuit voltage. As a result, several cells, usually at least three to four cells, have to be stacked in series to power an application, which makes flexible construction in small scale difficult.

The present invention provides a fuel cell like technology with a high open-circuit voltage, which enables the construction of small-scale power sources with one to two cells only, easily providing a flexible structure.

SUMMARY OF THE INVENTION

An object of the present invention is to provide an electrochemical cell that is small, thin and has a flexible structure. The object of the present invention is achieved by an electrochemical cell which is characterized by what is stated in the independent claim. The preferred embodiments of the invention are disclosed in the dependent claims.

The inventors of the present invention discovered, surprisingly, that small, thin and mechanically flexible electrochemical cells can be provided by combining a metal-based anode with an enzyme-catalyzed cathode.

The advantage of the solution of the present invention is that the electrochemical cells of the invention have a high open-circuit voltage desired and higher power/current density compared to those of the known electrochemical cells utilizing enzyme catalyst. In addition, they are characterized by a simple structure employing no toxic or harmful materials. The electrochemical cells of the invention can thus be disposed easily with normal household waste. An additional advantage is that the electrochemical cells of the invention can easily be prepared by the generally known printing and coating methods, like screen printing technique, with low cost at industrial scale.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a general picture of an electrochemical cell of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to an electrochemical cell comprising an integrated metal-based anode and enzyme-catalyzed cathode. Figure 1 illustrates a general structure of an electrochemical cell of the invention. An anode part of the electrochemical cell comprises an anode current collector 1 and an anode paste 2 disposed on the anode current collector. A cathode part comprises a cathode current collector 5 and a cathode paste 4 disposed on the cathode current collector. The anode and cathode parts are separated from each other by a separator layer 3.

As in a standard electrochemical cell, the anode is the site for an oxidation reaction of a substrate with a concurrent release of electrons, and the cathode is the site for a reduction reaction of the oxidant. When the cell is connected to a power consuming device, a continuous flow of electrons from the anode to cathode is provided where the electrons are used to reduce an oxidant through an external circuit and a continuous flow of ions between anode and cathode ionic currents simultaneously. The oxidant can be oxygen or a proper oxidant. In the case of oxygen, it is taken from air, which means that the performance of the electrochemical cell of the invention is not limited by an oxidant supply. In this manner, the electrochemical cell of the invention acts as an energy source for electrical load.

1. Anode

An anode used in the electrochemical cell of the present invention comprises an anode current collector and an anode paste. In one embodiment of the invention, the anode paste comprises metal powder, an electrolyte and a binder. The metal powder according to the invention is an anode active material providing electrons. The metal powder can be selected from the group of non-toxic metals appearing low in the electrochemical series having lower potential. These non-toxic metals include zinc, aluminium, iron and titanium. In a preferred embodiment of the invention, the metal powder is of zinc.

Generally, an electrolyte is a substance that facilitates the release of electrons at the electron conductor. The electrolyte is incorporated in the anode paste to provide an adequate ionic current and both anode and cathode electrode reactions. Suitable electrolytes useful in the present invention include any kind of inorganic non-toxic salt solutions, acids and bases, for example NaCl, $ZnCl_2$, NH_4Cl, HCl, KOH, $Zn(Ac)_2$ and other materials known to those skilled in the art. The preferred electrolytes are $ZnCl_2$ and KOH, more preferably $ZnCl_2$.

In another embodiment of the invention, the anode paste further comprises one or more additives. In accordance with the invention, an additive is used to improve the performance of the electrochemical cell, for example by way of inhibiting corrosion of the metal powder used in the anode paste. An exemplary additive includes zinc oxide when zinc is used as metal powder. Also ammonium chloride can be used for optimizing the performance of the electrochemical cell.

In a further embodiment of the invention, the anode paste further comprises carbon powder. The carbon powder can be graphite powder, carbon black powder or the like, preferably graphite powder. In accordance with the invention, the purpose of using carbon powder in the anode paste is to increase the capability of maintaining moisture in the anode, which further improves the performance of the electrochemical cell.

In accordance with the invention, a binder is used to hold the metal powder, electrolyte, and additive and carbon powder, if present, together. Binders that can be used in the present invention include polyvinyl alcohol (PVA), polyacrylic acid (PAA), carboxymethyl cellulose (CMC), starch and other materials known to those skilled in the art.

In accordance with the invention, the anode paste is disposed on the surface of the anode current collector. In a specific embodiment of the invention, the paste is disposed on the surface by printing or coating method, like screen printing method, as a thin layer form.

The anode current collector used in electrochemical cell of the invention can be made of various electric conductive materials. Suitable conductive materials are typically non-corroding and can include, for example, carbon ink, graphite foil, carbon fabric, as well as other materials known to those skilled in the art. In the present invention, the current collector is preferably in a form of a film.

It should be noted that in the present invention, no catalysts are used in the anode of the electrochemical cell of the present invention. Accordingly, zinc is not a catalyst but a substrate providing electrons. The redox reaction taking place at the anode can be described as follows:

$$M \rightarrow M^{n+} + ne$$

where M means a metal. If the metal is zinc, the equation is

$$Zn \rightarrow Zn^{2+} + 2e$$

2. Cathode

A cathode used in the electrochemical cell of the present invention comprises a cathode current collector and a cathode paste or ink. In one embodiment of the invention, the cathode paste comprises an enzyme catalyst, an electrolyte, an electron mediator, carbon powder and a binder. In another embodiment of the invention, the cathode ink comprises an enzyme catalyst, an electron mediator and electric conductive ink. For the purposes of this application, the term “cathode paste” means a combination of substances, which contains moisture. The term “cathode ink” means a combination of substances, which is dried after it is assembled. Generally, the terms “paste” and “ink” are concepts which are well known to those skilled in the art of electrochemical cells.

In order to provide an adequate electron transfer between the cathode current collector and enzyme active centre, and to improve the current densities of an electrochemical cell, an electron mediator, hereinafter mediator, is used in the cathode. The mediator is included in the paste or ink disposed on the cathode current collector. The mediator is a compound that can easily accept or donate electrons. Thus, mediator has an oxidized form that can accept electrons to form the reduced form. The reduced form can donate electrons to form the oxidized form. The mediator useful in the present invention include 4-hydroxybenzoic acid, 4-hydroxybenzylalcohol, 2,2’-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), 1-hydroxybenzotriazole, methionine, cysteine and reduced glutathione. Also other materials suitable for mediators known to those skilled in the art can be used. In a specific embodiment of the invention, ABTS is used as a mediator.

An electrolyte is provided in the cathode paste to assure ionic current in the electrochemical cell and a cathode reaction. Suitable electrolytes useful in the cathode paste include salt solutions, like a succinate buffer solution, $ZnCl_2$ and other materials known to those skilled in the art.

The carbon powder used in the cathode paste can be graphite powder, carbon black powder or the like, preferably graphite powder. In accordance with the invention, the main purposes of using carbon powder in the cathode paste are to increase the capability of maintaining moisture in the cathode and to increase the conductivity of the cathode paste due to less electric conductivity of the other components in the cathode paste. Moisture is needed for an enzyme to function properly.

A binder is used in the cathode paste to hold enzyme, mediator, electrolyte, and carbon powder together. Binders that can be used include those mentioned in context with the anode paste, like PVA, PAA and CMC. It should be noted that when a cathode ink is used in the cathode, no additional binder is needed to be introduced to the ink.

Like the paste present on the anode, the cathode paste or ink is disposed on the surface of the cathode current collector. In a specific embodiment of the invention, the cathode paste is disposed on the surface by printing or coating method, like screen printing method, as a thin layer form.

Cathode current collector used in the present invention is a permeable collector. Like the anode current collector, the cathode current collector can be made of various conductive materials. Suitable conductive materials are typically non-corroding and can include, for example, hydrophobic carbon ink, carbon cloth, carbon fabric, as well as other materials known to those skilled in the art. In the present invention, the current collector is preferably in a form of a film.

In accordance with the invention, the cathode is arranged for electroreducing an oxidant in the presence of an enzyme. In a preferred embodiment, the oxidant is gaseous oxygen originating from air. For the electroreducing reaction, oxygen diffuses from air into the cathode paste and dissolves into it. In another embodiment, the oxidant is a peroxide compound or cytochrome c. In the case where peroxide or cytochrome c is used, they are included in the cathode paste. When ink is used, the oxidant is brought into contact with the ink layer through a moisturized surface.

In accordance with the invention, an enzyme catalyzes a reduction reaction of an oxidant at the cathode using electrons provided by the anode. Exemplary enzymes for electroreduction of an oxidant include many types of oxidoreductases. According to the invention, the term oxidoreductase refers to an enzyme capable of catalyzing a reduction reaction of oxygen or peroxide to water, and a reduction reaction of cytochrome c from Fe^{3+} to Fe^{2+}. Potential oxidoreductases to be used in the present invention include laccases and other oxidases. In a preferred embodiment of the invention, the enzyme is oxygen oxidoreductase, like cytochrome c oxidase, Pseudomonas cytochrome oxidase, Rifamycin-B oxidase, 3-hydroxyanthranilate oxidase, O-aminophenol oxidase, L-ascorbate oxidase, Catechol oxidase and laccase. When peroxide is used as an oxidant, exemplary enzymes include cytochrome c peroxidase, catalases and peroxidases. When cytochrome c is used as an oxidant, the enzymes include L-ascorbate-cytochrome-b5 reductase and Ubiquinol-cytochrome c reductase.

In the present invention, the oxidoreductase type enzyme takes part in the redox reaction being capable of catalyzing a reduction reaction of an oxidant to water, when oxygen or peroxide is used as an oxidant, or to cytochrome c (Fe^{2+}), when cytochrome c Fe^{3+} is used as an oxidant. At the cathode, electrons originating from the anode flow into the cathode electrode. There, the electrons combine with an oxidized form of a mediator to produce a reduced form of the mediator. Next, the reduced form of the mediator reacts with an oxidized form of the enzyme to produce a reduced form of the enzyme and an oxidized form of the mediator. The reduced form of the enzyme then reacts with the oxidant to produce a reduced form of the oxidant and water. The above reaction course can be illustrated by the following equation for oxygen as an oxidant:

Mediator (oxidant) + electron $\rightarrow$ Mediator (reductant)

Mediator (reductant) + Enzyme (oxidant) $\rightarrow$ Mediator (oxidant) + Enzyme (reductant)

Enzyme (reductant) + O_2 $\rightarrow$ Enzyme (oxidant) + H_2O

In order to illustrate the redox reaction of a redox enzyme of the cathode part, an example is given below using laccase as a cathode enzyme.

4 benzenediol + O_2 = 4 benzosemiquinone + 2 H_2O

where benzenediol is the reduced form of the laccase and benzosemiquinone is the oxidized form of the laccase.

The anode and cathode of the electrochemical cell of present invention are separated from each other by a separator layer. Said layer is of any type of porous material, such as filter paper, capacity paper and various plastic films, for allowing protons flow through said separator layer. Several materials are suitable for the separative layer and are well known to those skilled in the art. In one embodiment of the invention, the separator layer contains an electrolyte, such as those mentioned as suitable in the anode paste and the cathode paste. When the cathode ink is used in the cathode, the separator layer contains an electrolyte.

The open circuit voltage of the electrochemical cell of the invention typically ranges from 1.3–1.5 V. The other operational parameters, such as the output power, depend on the physical dimensions of the electrochemical cell.

The electrochemical cell of the present invention may be used in applications that require an electrical supply. Especially, the electrochemical cells of the invention are useful in applications where small, thin and mechanically flexible power sources are required. However, the size of the cells is not limited to small, because printing technology can be applied to large areas as well. Enlarging the size of the electochemical cells of the present invention increases the output power, which may be useful in some applications, like in flexible display units attached to different kind of surfaces. The electrochemical cells of the invention can have a size of, e.g., 4 x 4 cm^2 and a thickness of about 1 mm. Examples of the suitable applications include, but are not limited to, intelligent labels, microsensors and RFID (Radio Frequency Identification) tag applications when it is desirable to extend the read distance and to enhance the independency of the position of a reader. There is increasing interest for this sort of applications.

EXAMPLES

This is an example of a "Zn – air" electrochemical cell. The anode paste comprises zinc powder, PVA as a binder, zinc chloride as an electrolyte and graphite powder. The cathode paste comprises laccase enzyme, ABTS as a mediator, both zink chloride solution and succinate buffer solution as an electrolyte, graphite powder and PVA as a binder. An oxidant used is oxygen from air. The separator between the anode and the cathode was filter paper from VWR International Inc. The anode collector was graphite foil and the cathode collector was carbon fabric. The cell size was 4 x 4 cm^2 and the thickness was about 1 mm.

The electrochemical cell as defined above was used to measure the open circuit voltage (max. open), current after 5 hours and 15 hours discharging, and total capacity. The testing runs were repeated four times. The results are shown in the table below.

	Open Voltage (mV) after one hour preparation	Current (mA) under 2000 ohm after 5 hours discharging	Current (mA) under 2000 ohm after 15 hours discharging	Total capacity (mAh) for 800 mV cutoff voltage
Cell 1	1423	0.5475	0.4237	8.31
Cell 2	1418	0.5421	0.4304	8.45
Cell 3	1384	0.5034	0.4193	7.24
Cell 4	1389	0.5053	0.4044	6.98
Average	1404	0.5246	0.4195	7.75

The average power produced from the tested cells was approximately 410 µW.

It will be obvious to a person skilled in the art that, as the technology advances, the inventive concept can be implemented in various ways. The invention and its embodiments are not limited to the examples described above but may vary within the scope of the claims.

Claims

1. An electrochemical cell using enzyme catalyst comprising:

a metal-based anode comprising an anode current collector and an anode paste;

a cathode comprising a cathode current collector and a cathode paste or ink including enzyme catalyst; and

a separator layer between said anode and cathode.

2. An electrochemical cell according to claim 1 wherein the anode paste comprises metal powder, an electrolyte and a binder.

3. An electrochemical cell according to claim 2 wherein the metal powder is selected from the group of non-toxic metals appearing low in the electrochemical series.

4. An electrochemical cell according to claim 3 wherein the metal powder is selected from the group consisting of zinc, aluminium, iron and titanium.

5. An electrochemical cell according to claim 4 wherein the metal powder is zinc.

6. An electrochemical cell according to any of claims 2 to 5 wherein the binder is PVA.

7. An electrochemical cell according to any of claims 2 to 6 wherein the electrolyte is an inorganic non-toxic salt solution, acid or base, such as NaCl, $ZnCl_2$, NH_4Cl, HCl, KOH, $Zn(Ac)_2$.

8. An electrochemical cell according to any of the preceding claims wherein the anode paste further comprises one or more additives, such as inhibitors, like zinc oxide.

9. An electrochemical cell according to any of the preceding claims wherein the anode paste further comprises carbon powder.

10. An electrochemical cell according to any of the preceding claims wherein the anode paste is disposed on the anode current collector as a thin layer by printing or coating method.

11. An electrochemical cell as claimed in any of the preceding claims wherein the cathode paste including enzyme catalyst also comprises an electron mediator, electrolyte, carbon powder and a binder.

12. An electrochemical cell as claimed in any of claims 1 to 10 wherein the cathode ink including enzyme catalyst also comprises an electron mediator.

13. An electrochemical cell according to claim 11 or 12 wherein the enzyme is an oxygen oxidoreductase type enzyme selected from the group consisting of cytochrome c oxidase, Pseudomonas cytochrome oxidase, Rifamycin-B oxidase, 3-hydroxyanthranilate oxidase, O-aminophenol oxidase, L-ascorbate oxidase, Catechol oxidase and laccase.

14. An electrochemical cell as claimed in claim 13 wherein the enzyme catalyst is laccase.

15. An electrochemical cell as claimed in any of claims 11 or 14 wherein the electron mediator is 2,2'-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid).

16. An electrochemical cell as claimed in claim 11 wherein the electrolyte is an inorganic non-toxic salt solution, such as succinate buffer solution or $ZnCl_2$.

17. An electrochemical cell as claimed in claim 11 wherein the binder is PVA.

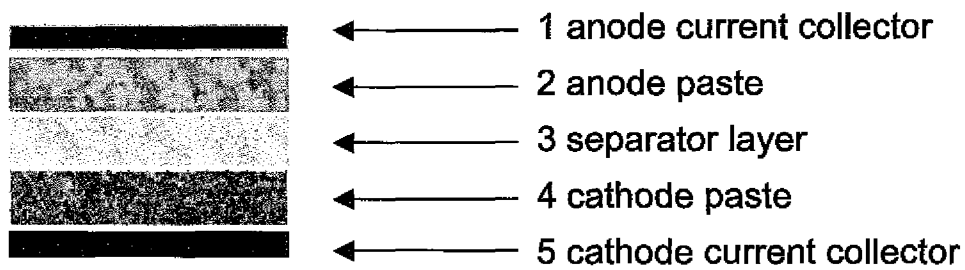
18. An electrochemical cell according to any of claims 11 or 17 wherein the cathode paste or ink is disposed on the cathode current collector as a thin layer by printing or coating method.

19. An electrochemical cell according to any of the preceding claims wherein the cathode is arranged for electroreducing oxygen, peroxide or cytochrome c as a cathode oxidant, preferably oxygen originating from air.

20. An electrochemical cell according to any of the preceding claims wherein the separator layer contains electrolyte, such as salt solutions, when cathode ink is used.

21. An electrochemical cell according to any of the preceding claims for use in applications requiring thin, flexible, low power source, like in intelligent labels, microsensors and RFID-tag applications.

Fig. 1


1 anode current collector
2 anode paste
3 separator layer
4 cathode paste
5 cathode current collector

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2007/050368

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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)

IPC8: H01M

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

FI, SE, NO, DK

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

EPO-Internal, WPI, EMBASE, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2006-93090 A (SONY CORP) 06 April 2006 (06.04.2006), (abstract), [online], Patent Abstract of Japan, Retrieved from EPOQUENET/BNS	1-21
A	WO 2006/009324 A1 (CANON KK et al.) 26 January 2006 (26.01.2006)	1, 11-21
A	US 2003/0099882 A1 (HAMPDEN-SMITH MARK J et al.) 29 May 2003 (29.05.2003)	1-10
A	US 2003/0113630 A1 (KAINTHLA RAMESH C et al.) 19 June 2003 (19.06.2003)	1-9

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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		AU 2002327651 A1	23/06/2003

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