Espacenet my patents list on 09-07-2016 11:27

7 items in my patents list
Displaying selected publications

Publication	Title	Page
WO2016092578 (A1)	DEVICE FOR PRODUCING HYDROGEN	2
EP1939968 (A1)	BIOLOGICAL POWER PLANT, AND METHOD OF...	18
US2013256149 (A1)	MICROBIAL ELECTROLYSIS CELLS AND METH...	70
US2010190039 (A1)	DEVICE AND METHOD FOR CONVERTING LIGH...	83
US2008213632 (A1)	LIGHT-POWERED MICROBIAL FUEL CELLS	90
EP1742288 (A1)	Microbial fuel cells for oxidation of...	103
US2012082868 (A1)	Floating Microbial Fuel Cells	121

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
16 June 2016 (16.06.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/092578 A1

(51) International Patent Classification:
C25B 1/10 (2006.01) *C02F 1/461* (2006.01)
C25B 9/00 (2006.01) *H01M 8/00* (2016.01)
H01M 8/16 (2006.01) *H01M 8/10* (2006.01)
H01M 8/1018 (2016.01)

(21) International Application Number:
PCT/IT2015/000298

(22) International Filing Date:
9 December 2015 (09.12.2015)

(25) Filing Language: Italian

(26) Publication Language: English

(30) Priority Data:
MI2014A002102 9 December 2014 (09.12.2014) IT

(72) Inventor; and
(71) Applicant : **LAVANGA, Vito** [IT/IT]; Via Terrazzano 85, 20017 Rho (MI) (IT).

(72) Inventor: **FARNE', Stefano**; Via Trasimeno 40/14, 20128 Milano (MI) (IT).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,

[Continued on next page]

(54) **Title**: DEVICE FOR PRODUCING HYDROGEN

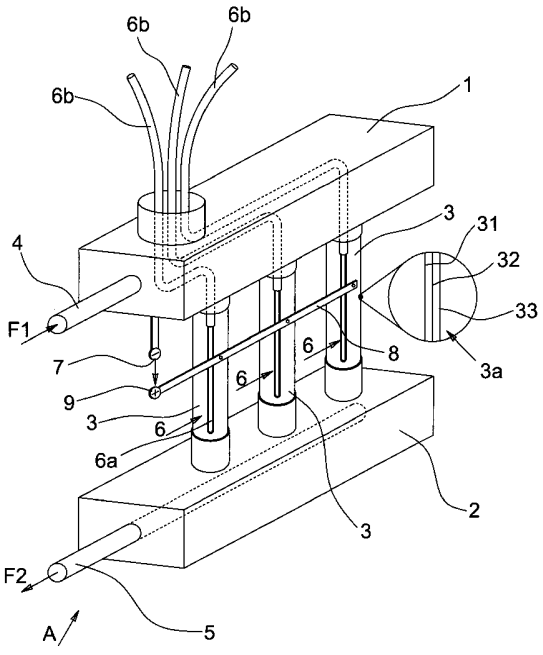


Fig. 1

(57) **Abstract**: This invention relates to a device for extracting, produce and convert into electric energy the hydrogen dissolved in a liquid mixture. Said device (A, B) is of the type able to produce hydrogen through the use of bacteria and it is characterized in that it includes: • a first manifold (1), in which a flow (F1) of said liquid mixture runs into; • a second manifold (2), from which a flow (F2) of said liquid mixture comes out; • one or more pipes (3) fitted to hydraulically connect said first (1) and second (2) manifold, so that said liquid mixture flows from said first manifold (1) to said second manifold (2); wherein the walls (3a) of said one or more pipes (3) include: • a first layer (31), made of metallic material, fitted to receive the bacterial consortia, said first layer (31) being electrically connected to a first terminal (7), that constitutes the anode of said device (A, B); • a second layer (32), including a proton exchange membrane (PEM - Proton Exchange Membrane), said membrane (32) having characteristics of solidity and water-tightness adequate to ensure the containment of said liquid mixture; • a third layer (33), made of metallic material, electrically connected to a second terminal (9) that constitutes the cathode of said device (A, B); the dissolved hydrogen oxidizing and giving electrons to said first metallic layer (31), that is negatively charged, and the residual protons diffusing through said PEM membrane, that constitutes said second layer (32) and spreading to the outside of said pipes (3).

WO 2016/092578 A1

SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

DEVICE FOR PRODUCING HYDROGEN

DESCRIPTION

This invention relates to a device to extract, to produce and to convert into electric energy the hydrogen dissolved in a liquid mixture.

It is strongly felt the need to have systems of general recovery of energy through the hydrogen vector, better if by distributed processes (in particular from urban and suburb territories) and related to the solution of other latent problems (wastes, with particular reference to the "wet" part), in particular when this is detrimental to other processes, which the methanogenesis in anaerobic digesters. This problem is faced by resorting, usually at environmental conditions suitable for the development of a bacterial consortium additional and capable to absorb hydrogen that determines small productions of methane. This determine significant problems of balances to be managed for chemical-physical conditions of the fluid on which you are working. This invention constitutes an innovation with respect to the current state of the art, allowing to overcome these problems in a simple and economical way.

In summary, in the current state it is not possible to convert the hydrogen dissolved in the liquid phase and at the same time to implement its production and consequently the correlated electric energy.

The object of this invention is to propose a device in accordance with claim 1, to extract, to produce and to convert into electric energy the hydrogen dissolved in a liquid mixture. Said device is of the type able to produce hydrogen through the use of bacteria and it is characterized in that it includes:

- a first manifold, in which a flow of said liquid mixture enters;
- a second manifold, from which a flow of said liquid mixture comes out;
- one or more pipes fitted to hydraulically connect said first and second manifold, so that said liquid mixture flows from said first manifold to said second manifold;

wherein the walls of said one or more pipes include:

- a first layer of metallic material, fitted to receive the bacterial consortia, said first layer being electrically connected to a first terminal, which constitutes the anode of said device;
- a second layer, including a proton exchange membrane (PEM - Proton Exchange Membrane), said membrane having characteristics of solidity and water-tightness sufficient to ensure the containment of said liquid mixture;
- a third layer of metallic material, electrically connected to a second terminal that constitutes the cathode of said device;

the dissolved hydrogen oxidizing and giving electrons to said first metallic layer, that is negatively charged, and the residual protons spreading through said PEM membrane and spreading to the outside of said pipes (3).

Other characteristics, such as for example to arrange the device in a watertight container and to activate it in steady state (Microbial Electrolsys Cell), to produce molecular hydrogen for later use or to activate the device using radiative spectrum fitted to the opposition of existing pathologies, will be the subject of the dependent claims.

The use of a device according to the invention allows, for example,:

- to extract the hydrogen dissolved in a liquid mass and to convert it into electric energy, during the hydrolytic and acidogenesis phase of the anaerobic digestion;
- extract the hydrogen dissolved in a liquid mass and to convert it into electric energy, during the phase of microalgae crops;
- to fight the onset of pathologies in a liquid mass through a fitted radiative spectrum, in depurative processes.

The invention will now be described for illustrative and not limitative purpose, according to a preferred embodiment and with reference to the enclosed drawings, wherein:

- Figure 1 shows a device according to the invention;
- Figure 2 shows a variant of the device according to the invention, to

take the extracted hydrogen.

With reference to fig. 1 with (A) it is indicated a device according to the invention, to extract and produce hydrogen from aqueous fluids and convert it into electric energy. Said device (A) is a fuel cell which is fitted to produce electric energy.

According to a preferred embodiment, said device (A) comprises a first manifold (1) and a second manifold (2) connected between them by a plurality of pipes (3), whose structure will be specified later on. Furthermore at least the first manifold (1) is preferably made of conductive material, since it will have to conduct electricity, as it will be specified in what follows.

The aqueous fluid in treatment, represented by the arrow (F1), runs into the first manifold (1) through a first pipe (4) and passing through the pipes (3), runs into the second manifold (2), from which it exits through a second pipe (5), the outlet flow being represented by the arrow (F2). In order to level out the flows in the pipes (3), said second pipe (5) extends in depth into the second manifold (2), realizing an attitude of reverse return.

In each of said pipes (3) are preferably present means fitted to spread a radiative spectrum including frequencies that are useful to the treatment of the aqueous fluid. Said means include, for example, a device (6) that makes use of side emitting optical fibers conforms to Italian patent application no. MI2014A002102 in the name of the same applicants.

Said optical fibers device (6) is able to broadcast frequencies, possibly taken from solar radiation, able to favour the biological reactions (red and of blue frequencies and InfraRed) and to fight the proliferation of bacteria and harmful viruses (UV frequencies).

The device (6) includes a diffuser (6a), made with side emitting optical fibers, that broadcast the radiation into the fluid in treatment and a part (6b), consisting of point-to-point optical fibers, which leads the signal from the generator to said diffuser (6a).

In the enlarged detail of fig. 1 it is shown the composition of the wall (3a) of one of the pipes (3). Starting from the inside of the pipe (3), said wall (3a)

includes:

- a first layer (31), made of metallic material and constituted for example by a stretched sheet, on which any bacterial consortia will be settled, said first layer (31) being electrically connected to said first hydraulic manifold (1), that constitutes the anode of a fuel cell (A);
- a second layer (32), including a proton exchange membrane (PEM - Proton Exchange Membrane), said membrane (32) having characteristics of solidity and water-tightness sufficient to ensure the containment of the fluid;
- a third layer (33), made of metallic material and constituted for example by a stretched sheet, electrically connected, by means of a metal bar (8) to the corresponding layers of the other pipes (3) that constitutes the cathode (9) of the fuel cell (A).

The device (A) has two modes of operation.

According to a first mode, in which there are specific bacteria on the first inner layer (31) of the wall (3a) of the pipes (3), the device (A) operates as a hydrogen (produced by bacteria) generator and as a hydrogen (obtained by electrolysis from the aqueous fluid in treatment) puller.

According to a second mode (not shown), in which said bacteria are not present, the device (A) only works as hydrogen (obtained by electrolysis from aqueous fluid in treatment) puller. In this case it is not necessary the presence of the optical fiber devices (6).

In case of operation according to said first mode, the bacteria present in the first layer (31) are stressed to the hydrogen release by the radiation coming from the diffusers (6a) placed inside the pipes (3). In practice the dissolved hydrogen oxidizes giving electrons to the first metal layer (31), which therefore is negatively charged and constitutes the anode of a fuel cell (A). The residual protons spread through the membrane PEM, which constitutes the second layer (32), and recombine outside with the oxygen of the air that will be reduced on the cathode that is constituted by the outside third metallic layer (33).

According to the described embodiment, the inner metallic layers (31) are

electrically connected with the first and the second manifold (1, 2), made of metal, while the external layers (33), made of metal too, are connected one each other by the metal bar (8). By the described electrical connections, it will be possible to obtain a potential difference between the terminals (7) and (9), from which it will be possible to take a direct current.

The passage of said current through a user device allows to close the circuit and this allows the cathode to favour the combination of hydrogen with oxygen, supporting the reaction.

During the transit through the device (A), the hydrogen content in the treated fluid it is reduced, said reduction being as greater than greater is the permanence time in the device (A). If it is desired to obtain a reduction a very high of the hydrogen content, the treatment can be repeated several times. This can be obtained by taking the fluid to be treated by means of taking and release, both targeted (through specific positioning of submersible pumps) and its delivery to the pipes (3). The substrate, depleted of hydrogen, then returns in the body of origin from which it is enriched again by the dilution of the original substrate and it is recycled, until the substrate reaches a preset load of hydrogen.

In fig. 2 it is shown a variant (B) of the invention, said variant (B) being fitted to produce molecular hydrogen. Said purpose is simply achieved by inserting the device (A) into a container (40), so as to avoid the contact with the air. In this way the protons, that spread through the membrane PEM, which constitutes the second layers (32) of the walls of the pipes (3), does not react with the oxygen and then will be reduced to diatomic hydrogen, which will be able to be taken through an outlet pipe (41). The described reaction is made possible by closing the circuit between the terminals (7) and (9).

The device according to the variant (B), can operate in reverse state, that is by applying suitable potential, it is stressed the specific permanent bacterial consortium, present on the first inner layer (31), to release hydrogen that is oxidized by the effect of said electrical potential, producing protons, which diffuse through the PEM of the second intermediate layer (32) and that, on the

third external layer (33), will be reduced to diatomic hydrogen, said reduction reaction occurring in the absence of oxygen.

In the case in which, for chemical or biological needs, it is necessary to reiterate or intensify the treatment of fluids, apart from the processes of efficiency in H2, the device (B) will be able to operate as an electrolytic cell, producing gaseous hydrogen on the cathode, that is in correspondence of the third outer layers (33). This is achieved by applying a potential difference to terminals (7) and (9) that causes a passage of direct current into the organic matrix in treatment inside the device (B).

The invention has been described for illustrative and not limitative purpose, according to two preferred embodiments. The person skilled in the art could devise several other embodiments, all included within the scope of protection of the enclosed claims.

CLAIMS

1. Device (A, B) to extract the hydrogen dissolved in a liquid mixture and to produce hydrogen by the use of bacteria, characterized in that it comprises:

- a first manifold (1), in which a flow (F1) of said liquid mixture runs into;
- a second manifold (2), from which a flow (F2) of said liquid mixture exits;
- one or more pipes (3) fitted to hydraulically connect said first manifold (1) and second manifold (2), so that said liquid mixture flows from said first manifold (1) to said second manifold (2);

wherein the walls (3a) of said one or more pipes (3) include:

- a first layer (31), made of metallic material, fitted to receive the bacterial consortia, said first layer (31) being electrically connected to a first terminal (7), that constitutes the anode of said device (A, B);
- a second layer (32), including a proton exchange membrane (PEM - Proton Exchange Membrane), said membrane (32) having characteristics of solidity and water-tightness adequate to ensure the containment of said liquid mixture;
- a third layer (33), made of metallic material, electrically connected to a second terminal (9) that constitutes the cathode of said device (A, B);

the dissolved hydrogen oxidizing and giving electrons to said first metallic layer (31), that is negatively charged, and the residual protons diffusing through said PEM membrane, that constitutes said second layer (32) and spreading to the outside of said pipes (3).

2. Device (A, B), according to claim 1, characterized in that said liquid mixture runs into said first manifold (1) through a first pipe (4) and comes out from said second manifold through a second pipe (5), said second pipe (5), extending in depth in said second manifold (2), realizing an attitude of reverse return and leveling the flows in said ducts (3).

3. Device (A, B), according to claim 1, characterized in that it includes means designed to spread a radiation spectrum in said liquid mixture, said spectrum including frequencies fitted to favour the biological reactions and/or to fight the proliferation of bacteria and harmful viruses.

4. Device (A, B), according to claim 3, characterized in that said means adapted to spread a radiation spectrum in said liquid mixture include a diffuser (6a), realized with side emitting optical fibers.

5. Device (A, B), according to at least one of claims from 1 to 4, characterized in that at least one of said manifolds (1, 2) is made of metallic material.

6. Device (A, B), according to claim 5, characterized in that said manifold (1 or 2) made of metallic material is electrically connected with said first terminal (7) and said first inner layer (31) of said wall (3a) of said one or more pipes (3).

7. Device (A, B), according to claim 1, characterized in that it has a metal bar (8) fitted to electrically connect said second terminal (9) with said third layer (33) of said wall (3a) of said one or more pipes (3).

8. Device (A, B), according to claim 1, characterized in that said first layer (31) and said third layer (33) of the wall (3a) of said one or more pipes (3), are made of stretched sheet.

9. Device (A), according to at least one of the claims from 1 to 8, characterized in that it includes means fitted to produce an electric current through a reaction with oxygen of said residual protons which, through said PEM membrane, diffuse to the outside of said pipes (3).

10. Device (A), according to claim 9, characterized in that said means fitted to produce an electric current by a reaction with oxygen of said residual protons, include:

- a connection of said metal internal layers (31) of said walls (3a) with a first terminal (7);
- a connection of said metal external layers (33) of said walls (3a) with a second terminal (9);

in such a way that the flowing of a direct current, obtained by connecting a user device to said first terminal (7) and second terminal (9), allows to close the circuit, promoting the combination of the hydrogen with the oxygen.

11. Device (B), according to at least one of the claims from 1 to 8, characterized in that it provides a container (40), fitted to contain said device (A), so as to avoid the contact with the air of the protons that come out from

said pipes (3) in such a way that said protons, not reacting with the oxygen, are reduced to molecular hydrogen.

5

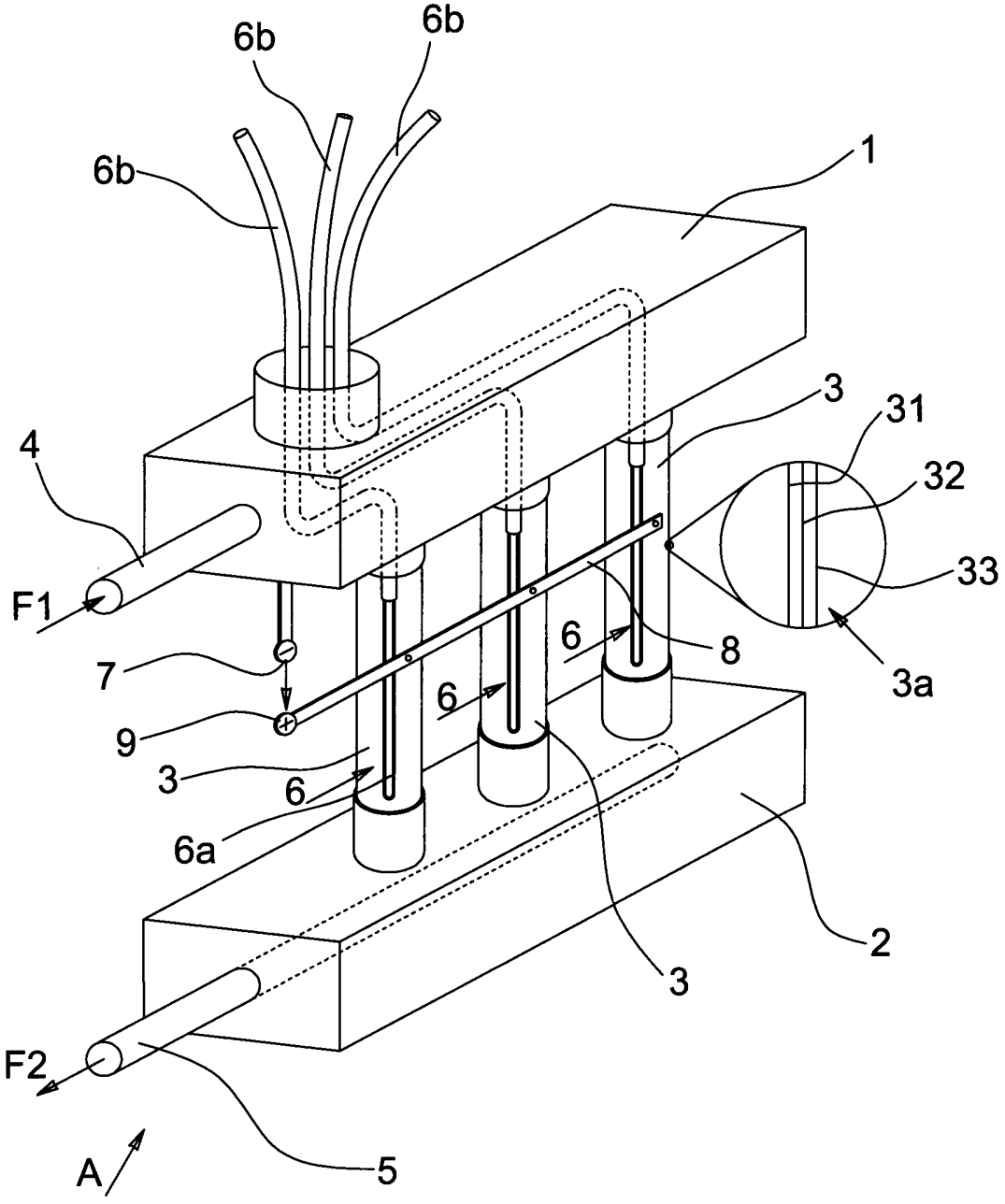


Fig. 1

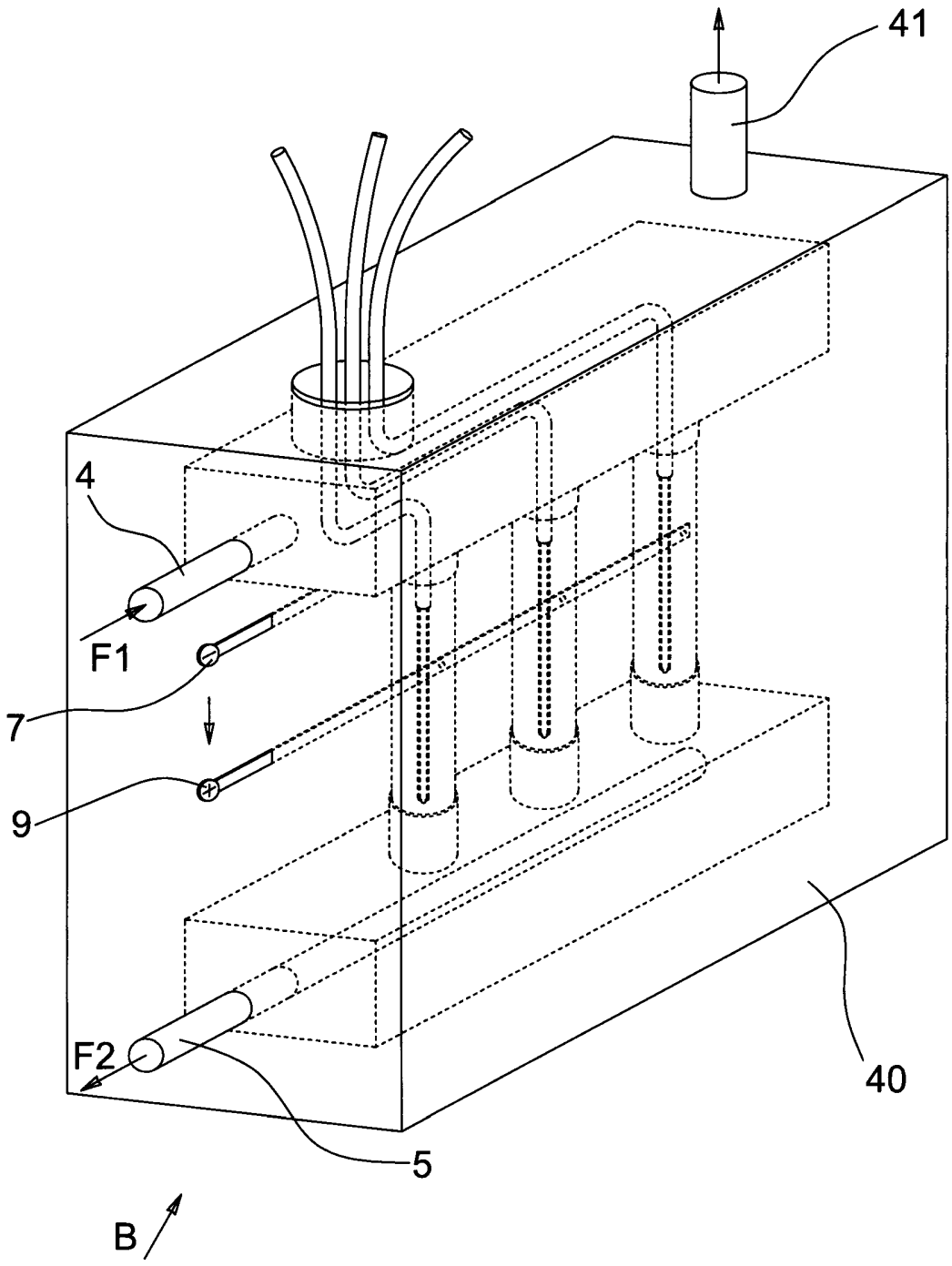


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/IT2015/000298

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25B1/10 C25B9/00 H01M8/16 H01M8/1018
ADD. C02F1/461 H01M8/00 H01M8/10

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)
C25B C02F H01M

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)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 939 968 A1 (EBARA CORP [JP]) 2 July 2008 (2008-07-02)	1,2,5-11
Y	claim 1 figures 2-4 paragraphs [0034], [0036], [0106], [0107], [0111] - [0114]	3,4
X	US 2013/256149 A1 (POPAT SUDEEP [US] ET AL) 3 October 2013 (2013-10-03)	1,2,5-11
Y	claims 1,3,8-10,14 figures 6,8 paragraphs [0036] - [0038], [0046]	3,4
Y	US 2010/190039 A1 (HAMELERS HUBERTUS VICTOR MARIE [NL] ET AL) 29 July 2010 (2010-07-29) claims 21,23-26,31,36 paragraphs [0026], [0028]	1-11

-/--

[X] Further documents are listed in the continuation of Box C.

[X] 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	Date of mailing of the international search report
27 April 2016	06/05/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Perednis, Dainius

INTERNATIONAL SEARCH REPORT

International application No
PCT/IT2015/000298

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008/213632 A1 (NOGUERA DANIEL R [US] ET AL) 4 September 2008 (2008-09-04) claims 1,4 figures 1-3	1-11
Y	EP 1 742 288 A1 (UNIV GENT [BE]) 10 January 2007 (2007-01-10) claims 1,4,10,12,21,23 figure 1 example 1	1-11
Y	US 2012/082868 A1 (HUANG YUELONG [US] ET AL) 5 April 2012 (2012-04-05) claims 1-3,8-11,20 paragraphs [0027] - [0030]	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IT2015/000298

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1939968 A1	02-07-2008	EP 1939968 A1	02-07-2008
		US 2009142627 A1	04-06-2009
		WO 2007037261 A1	05-04-2007
US 2013256149 A1	03-10-2013	NONE	
US 2010190039 A1	29-07-2010	BR PI0810389 A2	04-11-2014
		EP 2137782 A1	30-12-2009
		NL 2000598 C2	20-10-2008
		US 2010190039 A1	29-07-2010
		WO 2008127109 A1	23-10-2008
US 2008213632 A1	04-09-2008	US 2008213632 A1	04-09-2008
		WO 2008112371 A2	18-09-2008
EP 1742288 A1	10-01-2007	AU 2006269756 A1	18-01-2007
		CA 2614204 A1	18-01-2007
		EP 1742288 A1	10-01-2007
		EP 1902489 A2	26-03-2008
		US 2008220292 A1	11-09-2008
		WO 2007006107 A2	18-01-2007
US 2012082868 A1	05-04-2012	NONE	

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 939 968 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
02.07.2008 Bulletin 2008/27

(21) Application number: **06798360.1**

(22) Date of filing: **27.09.2006**

(51) Int Cl.:
H01M 8/16 *(2006.01)* ***B09B 3/00*** *(2006.01)*
C02F 11/00 *(2006.01)* ***C02F 11/02*** *(2006.01)*

(86) International application number:
PCT/JP2006/319152

(87) International publication number:
WO 2007/037261 (05.04.2007 Gazette 2007/14)

(84) Designated Contracting States:
DE NL

(30) Priority: **28.09.2005 JP 2005282767**
28.09.2005 JP 2005282772
28.09.2005 JP 2005282775

(71) Applicant: **EBARA CORPORATION**
Ohta-ku,
Tokyo 144-8510 (JP)

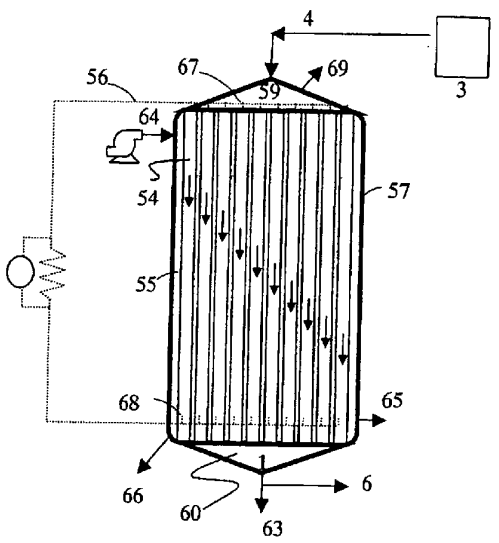
(72) Inventors:
- **SHIMOMURA, Tatsuo**
Fujisawa-shi, Kanagawa 2518502 (JP)
- **ADACHI, Masanori**
Fujisawa-shi, Kanagawa 2518502 (JP)
- **MIYA, Akiko**
Fujisawa-shi, Kanagawa 2518502 (JP)

(74) Representative: **Wagner, Karl H. et al**
WAGNER & GEYER
Patentanwälte
Gewürzmühlstrasse 5
80538 München (DE)

(54) **BIOLOGICAL POWER PLANT, AND METHOD OF TREATING ORGANIC SOLID CONTAMINANT-CONTAINING WASTE, METHOD OF TREATING ORGANIC HIGH MOLECULAR SUBSTANCE-CONTAINING LIQUID WASTE AND METHOD OF TREATING ORGANIC SUBSTANCE-CONTAINING LIQUID WASTE BY USING THE BIOLOGICAL POWER PLANT, AND APPARATUS FOR CONDUCTING THESE METHODS**

(57) Disclosed are a biological power generator comprising an anaerobic region containing microorganisms capable of growth under anaerobic conditions and an anode having an electron mediator immobilized thereon and having a standard electrode potential (E_0') in a range of -0.13 V to -0.28 V at pH 7, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region, as well as a method of treating organic waste by making use of the biological power generator.

FIG. 3



EP 1 939 968 A1

Description

TECHNICAL FIELD

[0001] The present invention relates to a technology for treating wastewater and other waste that contain organic substances such as organic solid pollutants and organic polymeric substances (which are collectively named "organic waste"), as exemplified by livestock waste, wastewater, liquid waste, night soil, food waste, and sludge.

[0002] The present invention also relates to a technology in which an oxidation reduction reaction between organic matter in organic waste and oxygen in air is separated into an oxidation reaction involving anaerobic microorganisms and a reduction reaction of involving oxygen, to thereby generate electricity, as well as to a technology for treating wastewater and other waste by making use of a resulting action by which a feed under treatment is decomposed.

BACKGROUND ART

[0003] In the treatment of wastewater containing organic pollutants, widespread use has conventionally been made of aerobic biological processes. However, this method is not only energy-consuming but also presents a big problem with regard to disposal of excess sludge that contains large amounts of difficult-to-decompose organic matter. In contrast, to treat wastewater containing organic pollutants at high concentrations and organic sludge, much use of the anaerobic system has conventionally been made. This system has several advantages including: absence of a need to apply external power for aeration, thus leading to lower energy consumption; less production of excess sludge, thus resulting in lower costs of treatment; and, capability to recover methane gas which is useful as an energy resource.

[0004] Being the primary component of natural gas, methane is a fuel of good quality but since it is gaseous at ordinary temperature and pressure, it must be stored in a large gas tank; and in order to reduce its volume by pressure application or liquefaction, large or complicated equipment and a large amount of energy are required. Methane obtained by anaerobic treatment of organic wastewater or waste may be burned in a boiler and the like, but in the current situation, it is not assured that the resulting thermal energy will be effectively utilized. On the other hand, electrical power is a highly convenient form of energy which not only can be utilized to power various types of machines and equipment but can also be transported over a long distance.

[0005] To produce electrical power from fuels such as methane, a gas engine or turbine is conventionally used which converts chemical energy of the fuel to electrical energy via mechanical energy. But the efficiency of such methods varies depending on a scale of output power. For example, in a gas engine, in a case that large equipment with an output power of 2 MW, efficiency of conversion from the fuel's chemical energy to electrical energy is about 40%, whereas in small equipment with an output power of about 10 kW has a 20-25% efficiency. In a case of a gas turbine, equipment having a capacity of 100 MW has an efficiency of 30-35%, while that in the 1 MW class has an efficiency of 25-35%, and a micro-gas turbine with an output power of 30 kW has an efficiency of 15-30%. Thus, gas engines and turbines with smaller scales of output power have only low efficiency of conversion to electric power. Taking into allowance equipment maintenance and management costs, it is substantially difficult to recover energy without using large-scale equipment.

[0006] In recent years, fuel cell technology capable of direct conversion of a fuel's chemical energy to electric power has been making progress. The solid polymer electrolyte fuel cell (PEFC) which is the closest to commercial usability is capable of conversion to electric power at an efficiency of as high as 35-40% even in small equipment of 1 kW, and holds promise for use in many fields as decentralized power generating equipment. Since the efficiency of energy recovery with methane resulting from anaerobic treatment of organic wastewater and waste is about 60-70%, a system using the fuel cell is expected to offer an efficiency in electric power recovery of about 20-30%. However, in the case where a biogas obtained by anaerobic treatment of organic wastewater and waste is used for the starting material, the catalyst which is the key to power generation with the PEFC is poisoned by hydrogen sulfide or ammonia gas, and these impurities must be removed from the biogas to a level of 1 ppm or lower. The catalyst is also contaminated with carbon monoxide, and the carbon monoxide that is generated when methane is reformed to hydrogen has to be removed from the reformed gas to a level of 10 ppm or lower.

[0007] A method that makes use of microorganisms to produce electric current has been reported, in which electrons from an electron donor around an anode are imparted to an electron acceptor (mainly dissolved oxygen) around a cathode, with the anode and cathode being electrically connected to make a circuit, whereby an electric current is obtained (Patent Documents 1, 2 and 3). In another case, a method has been proposed to draw electrons efficiently by keeping microbes "starving" as they are constantly fed an insufficient amount of organic matter (Patent Document 4). In yet another case, a process for producing enzyme electrodes has been proposed, in which a redox compound as an electron mediator for an oxidizing-reducing enzyme is immobilized on an electrode (Patent Document 5). As a microbial cell technology utilizing an electron mediator, a method has been proposed, in which a hydrous organic substance or a decomposition product thereof is used as a substrate and an oxidation-reduction reaction between the substrate and

oxygen is separated into an oxidation reaction by anaerobic microorganisms and a reduction reaction of oxygen, to thereby generate electricity (Patent Document 3 and Non-Patent Documents 1-3).

[0008] However, those methods are subject to a problem that the standard electrode potentials of the electron mediators they use do not overlap with the standard electrode potentials of final electron accepting substances for anaerobic microorganisms commonly used in the microbial cell reaction, and fail to form an effective potential cascade. The following Table 1 shows electron mediators proposed to date and their standard electrode potentials.

[0009] [Table 1]

Table 1 Standard Electrode Potentials of Various Electron Mediators

	Electron Mediator	Standard Electrode Potential E_0' (V)
A	Thionine	+0.064
B	Brilliant Cresyl Blue	+0.047
C	NAD^+	-0.32
D	Neutral Red	-0.325
E	Benzyl Viologen	-0.36
F	Methyl Viologen	-0.36
G	Ethyl Viologen	-0.45

[0010] Sulfur reducing bacteria and iron oxide(III) reducing bacteria, which are the anaerobic microorganisms employed in the common biological cell reaction use sulfur and iron as their respective final electron accepting substances, and the following Table 2 shows their respective standard electrode potentials.

[0011] [Table 2]

Table 2 Standard Electrode Potentials of Final Electron Accepting Substances for Anaerobic Microorganisms

Final Electron Accepting Reaction	Standard Electrode Potential E_0' (V)
O_2/H_2O	+0.82
Fe(III)/Fe(II)	+0.20
S(O) /H_2S	-0.28

[0012] As can be seen from Table 2, the terminal reducing enzyme (sulfur reducing enzyme) in the electron transfer system possessed by sulfur reducing bacteria can reduce substances having a standard electrode potential of -0.28 V, whereas the terminal reducing enzyme (iron oxide (III) reducing enzyme) in the electron transfer system possessed by iron oxide (III) reducing bacteria can reduce substances having a standard electrode potential of +0.20 V. These terminal reducing enzymes are found in the outer membrane or periplasm of microorganisms and since they are capable of reducing extracellular iron oxide or zero valent sulfur, these enzymes can be effective catalysts for efficient biological power generation. However, as shown in Table 1, the standard electrode potentials of the electron mediators proposed to date are such that all of the electron mediators A to G have standard electrode potentials lower than that required for reducing iron, and thus an effective potential cascade cannot be formed between the iron oxide (III) reducing enzyme, the electron mediator, and the anode. Similarly, the electron mediators C to G shown in Table 1 have standard electrode potentials lower than that required for reducing sulfur, so no effective potential cascade can be formed between the sulfur reducing enzyme, the electron mediator, and the anode. The electron mediators A and B shown in Table 1 have standard electrode potentials higher than that required for reducing sulfur, so it is theoretically possible to perform reduction with the sulfur reducing enzyme but given a potential difference greater than 0.3 V, biological electron transfer is highly likely to be problematic. In addition, in order to enhance efficiency of power generation, it is required to produce a greatest possible potential difference in the oxygen reducing reaction at the cathode. However, with high potentials of electron mediators, a potential difference greater than 0.3 V is lost, leading to a substantial energy loss.

[0013] Under these circumstances, an attempt has been made whereby in a microbial cell system using sulfur reducing bacteria, to improve an efficiency of electron transfer there is added to the anode compartment anthraquinone-2,6-disulfonic acid (AQ-2,6-DS) (Non-Patent Document 2). AQ-2,6-DS has a standard electrode potential of -0.185 V and is considered to be a suitable substance for forming an effective potential cascade between the sulfur reducing enzyme and the electron mediator. However, in the proposed system, AQ-2,6-DS was simply added to the liquid phase and not

immobilized on the anode (oxidizing electrode),and consequently its reactivity with the electrode was low, and the effect of its addition was no more than a 24% increase in the value of electric current. A further problem arises in the case of continuous power generation in that when the substrate solution in the anode compartment is replaced, the electron mediator is also discharged to the outside of the system, making it necessary for the electron mediator to be added constantly.

[0014] Since at least some of the microorganisms in the class of sulfur reducing bacteria and iron oxide (III) reducing bacteria are to some extent capable of transferringelectrons directly to an electrode even in an environment having no electron mediator, there has been proposed a microbial cell technology that does not use any electron mediator (Patent Document 6). This method has an advantage in that there is no need to retain any electron mediator within the system but, on the other hand, failure to perform efficient electron transfer from the microorganism to the electrode makes it impossible to increase the current density. As a result, it has been difficult, in practice, to obtain sufficient rates of power generation.

Patent Document 1: Official Gazette of JP 2000-133327 A
Patent Document 2: Official Gazette of JP 2000-133326 A
Patent Document 3: Official Gazette of JP 2002-520032 A
Patent Document 4: Specification of U.S. Patent 4652501
Patent Document 5: Official Gazette of JP 57-69667 A
Patent Document 6: Official Gazette of Japanese Patent 3022431 Non-Patent Document 1: Roller et al., 1984, Journal of Chemical Technology and Biotechnology 34B: 3-12
Non-Patent Document 2: Bond et al., 2002, SCIENCE 295:483-485 Non-Patent Document 3: Park et al., 2000, Biotechnology Letters 22:1301-1304
Non-Patent Document 4: Atsuharu Ikeda, Book of Abstracts for the 31st Seminar on New Ceramics, 2004.

DISCLOSURE OF THE INVENTION

MEANS FOR SOLVING THE PROBLEMS

[0015] In order to solve the object of obtaining sufficient rates of power generation, the present invention provides a power generating method characterized in that: one electrode which is an anode having an electron mediator immobilized thereon and having a standard electrode potential (E_0') in a range of -0.13 V to -0.28 V at pH 7 and another electrode which is a cathode are electrically connected to form a closed circuit; the anode is brought into contact with microorganisms capable of growth under anaerobic conditions, and into contact with a solution or suspension containing organic substances so that an oxidation reaction involving microorganisms that use the organic substances as an electron donor is allowed to proceed; the cathode and the solution or suspension are separated by an electrolyte membrane so that a reduction reaction that uses oxygen as an electron acceptor is allowed to proceed at the cathode; the oxidation reaction in the biological reaction system is thus promoted to generate electricity. The present invention also provides an apparatus for implementing this power generating method.

[0016] The present inventors have found that when wastewater or waste that contains solid or liquid organic pollutants, as exemplified by livestock waste, night soil, food waste, sludge, and wastewater (herein sometimes collectively referred to as "organic waste") are utilized as an electron donor for anaerobic microorganisms in the above-described biological power generating method and apparatus, an environmental impact of such organic wastewater and waste can be reduced and, at the same time, a chemical energy possessed by the organic matter in organic wastewater and waste can be directly converted to electric power without any need for an intervening energy converter, and also without any need for peripheral equipment such as a gas tank or reformer, whereby an added advantage is realized such that a treatment is also provided for purifying waste-containing organic pollutants.

[0017] The object of the present invention is to provide a treating method and apparatus that employ the above-mentioned biological power generating technology to ensure that an environmental impact of organic waste can be efficiently reduced while, at the same time, electrical energy is obtained.

[0018] More specifically, the object of the present invention is to provide a treating method and apparatus which, when treating organic solid pollutant-containing waste by utilizing biological power generating technology, are capable of efficiently converting organic solid pollutants to solubilized organic substances that are relatively easier to treat.

[0019] Another object of the present invention is to provide a treating method and apparatus which, when used for treating organic solid pollutant-containing waste in utilizing biological power generating technology, are capable of efficiently converting organic polymeric substances to organic substances that have been reduced in molecular weight, and which are easier to treat.

[0020] A further object of the present invention is to provide a method and apparatus for treating organic pollutants, by which the treated water as obtained from a biological power generator is further treated to ensure that a biological

oxygen demand (BOD) of less than 120 mg/L which is the uniform standard for emission (daily average) specified by the Water Pollution Prevention Law can be achieved consistently.

[0021] The present invention relates to a technology for treating waste and wastewater containing organic substances such as organic solid pollutants or organic polymeric substances (organic waste) by making use of a biological power generator and it particularly relates to a technology for treating organic waste by decomposing organic substances while generating electric power by an oxidation-reduction reaction between organic substances in the organic waste and oxygen in the air being separated into an oxidation reaction by anaerobic microorganisms and a reduction reaction of oxygen.

[0022] According to the present invention, it is provided that a biological power generator comprising an anaerobic region containing microorganisms capable of growth under anaerobic conditions and an anode having an electron mediator immobilized thereon and having a standard electrode potential (E_0') in a range of -0.13 V to -0.28 V at pH 7, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region, as well as a method of treating organic waste by making use of this biological power generator.

[0023] The anode having an electron mediator immobilized thereon is preferably such that at least one electron mediator selected from the group consisting of anthraquinone derivatives, naphthoquinone derivatives, benzoquinone derivatives, and isoalloxazine derivatives is immobilized on an electrode substrate; more preferably, the electron mediator is a substance selected from the group consisting of anthraquinone carboxylic acids (AQC), aminoanthraquinones (AAQ), diaminoanthraquinones (DAAQ), anthraquinone sulfonic acids (AQS), diaminoanthraquinone sulfonic acids (DAAQS), anthraquinone disulfonic acids (AQDS), diaminoanthraquinone disulfonic acids (DAAQ DS), ethyl anthraquinones (EAQ), methyl naphtoquinones (MNQ), methyl aminonaphtoquinones (MANQ), bromomethyl aminonaphtoquinones (BrMANQ), dimethyl naphtoquinones (DMNQ), dimethyl aminonaphtoquinones (DMANQ), lapachol (LpQ), hydroxy(methylbutenyl) aminonaphthoquinones (AlpQ), naphthoquinone sulfonic acids (NQS), trimethyl aminobenzoquinones (TMABQ), flavin mononucleotide (FMN), and derivatives thereof, as exemplified by anthraquinone-2-carboxylic acid (AQ-2-C), 1-aminoanthraquinone (AAQ), 1,5-diaminoanthraquinone (1,5-DAAQ), anthraquinone-2-sulfonic acid (AQ-2-S), 1,5-diaminoanthraquinone-2-sulfonic acid (1,5-DAAQ-2-S), anthraquinone-2,6-disulfonic acid (AQ-2,6-DS), anthraquinone-2,7-disulfonic acid (AQ-2,7-DS), anthraquinone-1,5-disulfonic acid (AQ-1,5-DS), 1,5-diaminoanthraquinone disulfonic acid (1,5-DAAQDS), 2-ethyl anthraquinone (2-EAQ), 2-methyl-1,4-naphthoquinone (2-M-1,4-NQ), 2-methyl-5-amino-1,4-naphthoquinone (2-M-5-A-1,4-NQ), 2-bromo-3-methyl-5-amino-1,4-naphthoquinone (2-Br-3-M-5-A-1,4-NQ), 2,3-dimethyl-1,4-naphthoquinone (2,3-DM-1,4-NQ), 2,3-dimethyl-5-amino-1,4-naphthoquinone (2,3-DM-5-A-1,4-NQ), lapachol (LpQ), 2-hydroxy-3-(3-methyl-2-butenyl)-5-amino-1,4-naphthoquinone (AlpQ), 1,2-naphthoquinone-4-sulfonic acid (1,2-NQ-4-S), 2,3,5-trimethyl benzoquinone (2,3,5-TMABQ), flavin mononucleotide (FMN), and derivatives thereof.

[0024] The electrode material that forms the anode in the biological power generator is preferably exemplified by porous material having electrical conductivity and specific preferred examples include porous graphite, carbon paper, graphite cloth, graphite felt, activated carbon fibers, molded carbon black, molded carbon nanotubes, molding of vapor-deposited carbon fiber, etc.

[0025] To immobilize the above-mentioned electron mediators on the electrode, it is preferred to use immobilizing methods that will neither inhibit the oxidizing and reducing capabilities of the electron mediators nor cause significant variations in the standard electrode potentials of the electron mediators. Desirably, bonding between the electron mediator and the electrode takes such a form that it is stable and will not be readily decomposed in an aqueous environment. It is also desirable that the electron mediator and the electrode are bonded in such a form as to provide electrical conductivity. However, in so far as a distance between the electron mediator and the electrode is no more than 200 Å, they need not be bonded directly, since electrons are capable of moving such a distance, and, hence, electrical conductivity can be maintained. If desired, functional groups may be introduced into either the electron mediator or the electrode substrate, or both, to immobilize the electron mediator on the electrode. The electron mediator may first be polymerized by making use of electrolytic polymerization or chemical polymerization before it is immobilized on the electrode substrate. Alternatively, the electron mediator may be polymerized after it is immobilized on the electrode. If desired, electrically conductive fibers may be formed on the electrode and the electron mediator is then immobilized on the conductive fibers. As immobilizing methods that satisfy these conditions, bonding methods shown in the following Table 3 and Table 4 are preferably employed.

[0026] [Table 3]

Table 3 Method of Bonding Various Electrodes to Electron mediators

Electrode Material or Coating Material	Functional Group of Electrode		Functional Group of Electron Mediator	Bonding Mode
Graphite	Carboxyl group Carboxyl group		Amino group Amino group	Amide bonding or Imide bonding
	Amino group		Carboxyl group	Amide bonding
			Sulfonic acid group	Sulfonamide bonding
	Hydroxyl group		Bromomethyl group	Ether bonding
			Phosphoric acid group	Phosphate bonding
			Phosphonic acid group	Phosphonate bonding
Gold or Platinum	None		Thiol group (introduced to carboxyl group by ester bonding)	
			Thiol group (introduced to sulfonic acid group by ester bonding)	
			Thiol group (introduced to hydroxyl group by ether bonding)	Gold- or Platinum-sulfur bonding
			Thiol group (introduced to amino group)	
			Dithiol group (introduced to phosphoric acid group by diester bonding)	
Metal oxides (TiO_2, SnO_2 etc.)	Silane coupler modification			
		Amine-containing silane coupler	Carboxyl group	Amide bonding
			Sulfonic acid group	Sulfonamide bonding
		Halogen- containing silane coupler	Hydroxyl group	Ether bonding
			Amino group	C-N bonding
		Hydroxyl group-containing silane coupler	Phosphoric acid group	Phosphate bonding

[0027] [Table 4]

Table 4 Methods of Polymerizing Electron Mediators

System	Structure of electron transfer medium	Polymerization (layer formation) method	Method of hydrophilization after polymerization
a	Anthraquinone derivatives Naphthoquinone derivatives Benzoquinone derivatives	Nitro group introduced → reduced for conversion to amino → to the reaction system of b Carboxyl group or sulfonic acid group introduced → to the reaction system of c or d	Sulfonic acid groups introduced by means of fuming sulfuric acid, conc. sulfuric acid, chlorosulfonic acid, SO_3 gas, or sulfurous acid
b	(Di)aminoanthraquinone derivatives Aminonaphthoquinone derivatives Aminobenzoquinone derivatives	Electrolytic polymerization	
c	Anthraquinone carboxylic acid derivatives Anthraquinone (di) sulfonic acid derivatives Naphthoquinone sulfonic acid derivatives	Acid chloride formed → (sulfone)amide bonding to pyrrole →electrolytic polymerization	
d	Anthraquinone carboxylic acid derivatives Anthraquinone (di) sulfonic acid derivatives	Acid chloride formed → (sulfone)amide bonding to polyethyleneimine → adsorbed on the anode	

[0028] Accordingly, in order to immobilize the electron mediator on the electrode substrate in the present invention, a suitable bonding method may be selected from among the methods shown in Table 3 and Table 4 depending on a combination of the electrode substrate and electron mediator to be used.

[0029] In a power generator to be used in the present invention, at least part of the cathode is preferably made of an electrically conductive porous material, net-like or fibrous material that contain voids in their structure, with an interface between the water containing hydrogen ions, the air, and electrons, namely, a site where air (oxygen), hydrogen ions and electrons are enabled to be adjacent to one another, being constructed in these voids. In this way, efficiency of contact with oxygen in the air and water at the water surface can be enhanced to promote a reduction reaction (electrode reaction) of oxygen in air. For instance, if an electrically conductive porous material having fine pores and that has electrically conductive particles (e.g., carbon, inert metal, or metal oxide) bound thereto by means of a binder resin is used as a cathode, water can be effectively drawn up by capillarity, hydrophilization action at the surface, and so on, to form a water/air contact interface within the fine pores, whereupon oxygen in the air and in the water make efficient contact to promote a reduction reaction of oxygen. The electrode substrate for use as the cathode is preferably exemplified by porous graphite, carbon paper, graphite cloth, graphite felt, activated carbon fibers, molded carbon black, molded carbon nanotubes, moldings of vapor-deposited carbon fiber, etc.

[0030] Furthermore, it is preferred that a catalyst comprising an alloy or compound containing at least one species selected from among platinoid elements, silver and transition metal elements is supported on the cathode and this contributes to promoting the reduction reaction (electrode reaction) of the oxygen in the air. The term "platinoid elements" refers to platinum (Pt), ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os) or iridium (Ir) and any of these is effective as an electrode catalyst. Those which support a silver powder doped with nickel (Ni), bismuth (Bi) or titanium oxide, or those having silver supported on furnace black or colloidal graphite, or those which use iron (Fe), cobalt (Co), phthalocyanine, hemin, perovskite, Mn_4N, a metal porphyrin, MnO_2, a vanadate or Y_2O_3-ZrO_2 composite oxide can also be preferably used as electrode catalysts.

[0031] An anion-exchange membrane may also be used as a diaphragm in the biological power generator of the present invention to separate the anaerobic region from the aerobic region. A specific preferred example is a hydroxide ion-exchange membrane having ammonium hydroxide groups. Examples that can also preferably be used as such an anion-exchange membrane include commercial products such as NEPTON AR103PZL-389 manufactured by IONICS, NEOSEPTA ALE manufactured by Tokuyama, and Selemion ASV manufactured by Asahi Glass. In this case, if anionic organic substances such as organic acids that occur in the anaerobic region pass through the diaphragm into the aerobic region (a phenomenon called "cross flow"), oxygen is consumed there and organic matter is oxidized in vain. While, at

the same time, aerobic microorganisms will proliferate in the aerobic region and thereby contaminate the cathode. Hence, the anion-exchange membrane to be used desirably works as a molecular sieve that will not easily transmit anions such as acetic acid that have molecular weights in excess of 60. An example of an anion-exchange membrane having such a property is NEOSEPTA ALE04-4A-0006 membrane manufactured by Astom.

[0032] Further examples of the diaphragm that can be installed in the biological power generator of the present invention are those having no functional groups, including MF (micro-filter) and UF (ultra-filter) membranes, porous filter media such as ceramics and sintered glass, and woven fabrics made of nylon, polyethylene, polypropylene, etc. These diaphragms having no functional groups are preferably such that they have pore diameters of no more than 5 μm and are gas-impermeable with no pressure applied. Examples that can be preferably used are PE-10 membrane manufactured by Schweiz Seidengazefabrik and NY1-HD membrane manufactured by Flon Industry.

[0033] In the biological power generator to be used in the present invention, the anode and the cathode are electrically connected to form a closed circuit. On the other hand, to exploit a reducing capability of organic substances as electrical energy without waste, the two electrodes must be separated to prevent contact occurring between the organic substances and oxygen in the air, so that the organic substances will not consume their reducing capability upon contact with the oxidant (the substance to be reduced), namely, oxygen in the air. To satisfy these conditions simultaneously, the cathode is desirably separated from electrode-active microorganisms and the solution or suspension containing the organic substances by use of a diaphragm, for instance, a solid polymer electrolyte membrane. By adopting this structure, the cathode can readily contact with oxygen in the air while, at the same time, supply of hydrogen ions to and from the cathode or discharge of hydroxide ions can be achieved via water in the diaphragm. In addition, the diaphragm is preferably such that a minimal amount of oxygen in the air can permeate through it.

[0034] Examples of the diaphragm that are preferably used include a perfluorinated ion-exchange membrane (cation-exchange membrane) with sulfonic acid groups that is hydrophilic and has high cation-exchange capability and a hydroxide ion-exchange membrane (anion-exchange membrane) having a quaternary ammonium salt. A perfluorinated ion-exchange membrane that has only the backbone chain fluorinated and an aromatic hydrocarbon membrane may be utilized as less costly diaphragms. Examples that can preferably be used as such ion-exchange membranes include commercial products such as NEPTON CR61AZL-389 manufactured by IONICS, NEOSEPTA CM-1 or CMB manufactured by Tokuyama, Selemion CSV manufactured by Asahi Glass, NEPTON AR103PZL manufactured by IONICS, NEOSEPTA AHA manufactured by Tokuyama, and Selemion ASV manufactured by Asahi Glass. The cation-exchange membrane can be used to ensure that the hydrogen ions and water that are necessary to reduce oxygen at the cathode are supplied from the anode to the cathode, and the anion-exchange membrane can be used to ensure that the hydroxide ions generated from the reaction between water and oxygen are supplied from the cathode to the anode.

[0035] It is preferred that the biological power generator used in the present invention further includes a mechanism that controls the pH of the liquid under treatment within the anaerobic region (which may be preliminarily solubilized or reduced in molecular weight, as will be described later). An applicable pH control mechanism is a common pH control mechanism comprising a pH meter for measuring the pH of the liquid under treatment, a control mechanism for controlling the supply of an alkaline chemical based on the result of measurement with the pH meter, and an alkaline chemical reservoir for holding the alkaline chemical. By controlling a drop of the pH of the liquid under treatment within the anaerobic region, the reduced mediator at the anode can be prevented from suffering a drop in the rate of an oxidation reaction, and a large current density can be obtained even in a continuous operation. The pH within the anaerobic region is preferably maintained to within a range of 10.5 to 6.5, more preferably to a range of 9.5 to 6.5, and most preferably to a range of 9.0 to 7.5. By controlling the pH drop in such a way that the pH is maintained within these ranges, a drop in a rate of oxidation reaction at the anode can be inhibited. It to be noted also that many of the enzymes possessed by microorganisms have optimum pHs near neutrality, and that too strong an alkalinity may inhibit a reduction reaction of the microorganisms. An alkaline substance that can be used in the treating apparatus of the present invention to effect pH control within the anaerobic region of the biological power generator may be any substance that shows alkalinity in aqueous solution; and preferred examples include alkali metals, alkaline earth metals, as well as hydroxides thereof, salts consisting of a strong base and a weak acid, and ammonia. Also applicable are substances of high alkalinity that show a neutral to weakly alkaline pH in aqueous solution, but whose aqueous solutions have a buffer action. Preferred examples include borates, phosphates, carbonates, and the like. When the substances mentioned above are to be used as alkaline substances, two or more of them may be added simultaneously.

[0036] Anaerobic microorganisms that can be used within the anaerobic region of the biological power generator in the present invention are desirably microorganisms that can transfer electrons to an extracellular substance so as to permit final electron transfer to the electrode (such microorganisms are hereinafter referred to as "electrode-active microorganisms"). Preferred examples of such electrode-active microorganisms with respect to the anode include sulfur S(0) reducing bacteria, iron oxide(III) Fe(III) reducing bacteria, manganese dioxide (MnO_2) reducing bacteria, and dechlorinating bacteria. Particularly preferred examples of such microorganisms include Desulfuromonas sp., Desulfitobacterium sp., Clostridium thiosulfatireducens, Acidithiobacillus sp., Geothrix sp., Geobacter sp., and Shewanella putrefaciens. In particular, sulfur-reducing bacteria are such that their final electron acceptor sulfur has a very low standard electrode

potential at -0.28 V, so they can transfer electrons to electron mediators having lower potentials than iron oxide(III) reducing bacteria, and hence are advantageous in terms of energy. Microorganisms that have such sulfur-reducing activity and which are preferably used include, for example, Desulfuromonas sp., Desulfitobacterium sp., Clostridium thiosulfatireducens sp., and Acidithiobacillus sp. Many of the above-mentioned electrode-active microorganisms are known to be such that monosaccharides, for instance, glucose or low-molecular weight organic acids, for instance, lactic acid can be utilized as a substrate (Non-Patent Document 4).

[0037] The present invention also relates to an apparatus and a method for treating organic waste by making use of the above-described biological power generator.

[0038] A first aspect of the present invention which relates to the treatment of organic waste is especially characterized by conversion of organic solid pollutants to solubilized organic substances before they are fed into the biological power generator.

[0039] A second aspect of the present invention which relates to the treatment of organic waste is especially characterized by converting organic polymeric substances to organic substances reduced in molecular weight before they are fed into the biological power generator.

[0040] A third aspect of the present invention which relates to the treatment of organic waste is characterized by including a post-treatment in which the primary treated water as obtained by primary treatment with the biological power generator is further treated.

<Treatment for Solubilizing Organic solid pollutant-containing Waste>

[0041] According to the first aspect of the present invention for treating organic waste, there is provided a method of treating organic solid pollutant-containing waste by making use of a biological power generator comprising an anaerobic region containing microorganisms capable of growth under anaerobic conditions and an anode having an electron mediator immobilized thereon and having a standard electrode potential (E_0') in the range of -0.13 V to -0.28 V at pH 7, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region, characterized by comprising: a solubilizing step in which the organic solid pollutants in the organic solid pollutant-containing waste are solubilized to form a solubilized liquid under treatment which contains solubilized organic substances; and a biological power generation step in which the solubilized liquid under treatment is fed into the anaerobic region of the biological power generator so that the oxidization reaction by the microorganisms which use the solubilized organic substances within the anaerobic region as an electron donor and the reduction reaction which uses the oxygen within the aerobic region as an electron acceptor are allowed to proceed to thereby reduce a pollution load in the solubilized liquid under treatment while generating electricity.

[0042] The organic solid pollutant-containing waste may be any wastewater and waste that contain solid organic matter and examples include residues from food processing such as wastewater from food processing plants, coffee grounds, waste brewer's yeast, and bean curd refuse, as well as leftover food (garbage), waste paper, animal waste, night soil, and excess sludge from water treatment facilities. These organic solid pollutant-containing waste may be immediately subjected to the solubilizing treatment but if desired, the organic solid pollutant-containing waste may be preliminarily subjected to solid-liquid separation and the resulting liquid fed into the anaerobic region of the biological power generator or, alternatively, they may be treated to have a smaller molecular weight and only the solids subjected to the solubilizing treatment.

[0043] Therefore, the treatment method under consideration comprises solubilizing organic solid pollutants in organic solid pollutant-containing waste into solubilized organic substances such as soluble substances, suspendable substances (suspension) or slurries, feeding the anaerobic region of the biological power generator with the liquid under treatment which contains the thus solubilized organic substances (hereinafter referred to as the "solubilized liquid under treatment"), and allowing the solubilized organic substances to act as a substrate for electrode-active microorganisms. In the present invention, "solubilized organic substances" refers to a solute that cannot be easily separated from a medium, and it is intended to embrace a solute in a solution but also a dispersoid in a dispersion, suspended matter in a suspension, and fine solids in a slurry. The degree of solubilisation can be expressed in terms of an increase in COD_{Cr} concentration of the soluble fraction of the liquid under treatment as compared with an initial level before the solubilizing treatment (which is a supernatant obtained by a centrifugal operation at 10000 revolutions per minute for 10 minutes); preferably, the organic substances can be said to have been solubilized when the COD_{Cr} concentration has increased by at least about 20%.

[0044] In the treatment method of the present invention, the solubilizing treatment is preferably performed by subjecting the organic solid pollutant-containing waste to at least one method selected from among mechanical crushing, physical treatment, thermal treatment, acid or alkali treatment, oxidizing treatment, and hydrothermal electrolytic treatment. For mechanical crushing treatment, a method such as crushing on a mill or stone mortar or crushing by sonication can preferably be used. For physical treatment, a method such as steaming or blasting can preferably be used. For the thermal treatment, a heat treatment may be applied in an atmosphere at ordinary pressures within the range of 80°C to

300°C, preferably in the range of 100°C to 300°C, most preferably in the range of 150°C to 250°C, for 20 minutes to 300 minutes, preferably for 20 minutes to 150 minutes, most preferably for 25 minutes to 60 minutes. For hydrothermal electrolytic treatment, there can be used a method in which a direct current in a quantity of no more than one half the amount of electricity that is required to generate oxygen equivalent to the chemical oxygen demand (COD) of the organic solid pollutant-containing waste by water electrolysis is applied at a temperature not lower than 100°C but not above the critical temperature of the organic solid pollutant-containing waste, and under a pressure sufficient to maintain the liquid phase. In addition, there can be used a method in which a chemical treatment such as acid/alkali treatment, ozone treatment, hypochlorous acid treatment or hydrogen peroxide treatment, as appropriately chosen depending upon a nature of the organic solid pollutants, is applied to improve their solubility in the solvent.

[0045] In the case of relying upon mechanical treatment or physical treatment, the organic solid pollutants are reduced to fine particles that have an increased surface area to bring about enhanced contact with the extracellular enzyme from the electrode-active microorganisms. In a case where excess sludge from the aerobic biological treatment vessel or the like is used as the organic solid pollutants, cells in the excess sludge are disrupted by a solubilizing treatment such as mechanical treatment or physical treatment so that soluble substances (solute) within the cells dissolve in the liquid under treatment (solvent), thus becoming susceptible to the decomposing action of the electrode-active microorganisms. In the case of solubilizing treatment by chemical treatment or thermal treatment, not only is solubility of the organic solid pollutants improved but they can also be converted to substances of an even smaller molecular weight, thus becoming more susceptible to a decomposing action of the electrode-active microorganisms. In a case where the organic solid pollutant-containing waste is sewage sludge or some other substance that has sufficient fluidity to be pumpable and which is comparatively homogeneous, solubilizing treatment can be carried out using a hydrothermal electrolytic treatment that performs electrolysis in a subcritical state (a hydrothermal electrolytic method and apparatus; see the pamphlet of WO 99/07641). In the hydrothermal electrolytic treatment, those difficult-to-decompose chromaticity components which are commonly found in thermal treatment of organic wastewater and the like to present a problem can be decomposed (see the official gazette of JP 2003-290740 A) and, at the same time, difficult-to-decompose organic matter can be converted to organic acids of even smaller molecular weight, thus leading to an improvement in a resulting quality of the treated water.

[0046] In the treatment method of the present invention, after the solubilizing step but before the solubilized liquid under treatment is fed into the biological power generator, a biological treatment that makes use of the metabolic reaction of anaerobic microorganisms or an enzyme treatment that makes use of the decomposing reaction by an enzyme, or the like may be applied to ensure that the polymeric substances in the solubilized liquid under treatment are converted to substances of an even smaller molecular weight. By performing this treatment for smaller molecular weight substances, the decomposing reaction by anaerobic microorganisms in the anaerobic region of the biological power generator proceeds with greater ease, contributing to an improvement in both treatment efficiency and power generation efficiency.

[0047] In addition, the treatment of the present invention may be so adapted that the treated water from the biological power generator is subjected to an aerobic microbial treatment as ordinarily carried our in treatment of water. If desired, part or all of the excess sludge resulting from the aerobic microbial treatment may be returned to the solubilizing step. What is more, the treated water from the biological power generator may be subjected to a post-treatment such as flocculation and precipitation, filtering through activated carbon, phosphate removal, denitrification, or sulfate reduction.

[0048] In the treatment method of the present invention, the solubilized liquid under treatment is subjected to a step of biological power generation by microorganisms capable of growth under anaerobic conditions (electrode-active microorganisms). In the biological power generation step, the oxidation reaction of the microorganisms which use the solubilized organic substances as an electron donor in the solubilized liquid under treatment that has been fed into the anaerobic region of the biological power generator, and the reduction reaction which uses the oxygen in the aerobic region as an electron acceptor are allowed to proceed to thereby reduce the pollution load in the solubilized liquid under treatment while generating electricity. In the biological power generation step, the solubilized liquid under treatment is controlled under conditions that can maintain activity of the electrode-active microorganisms occurring in the anaerobic region. For example, by controlling the drop of the pH of the solubilized liquid under treatment within the anaerobic region, the reduced mediator at the anode can be prevented from suffering a drop in the rate of oxidation reaction and a large current density can be obtained even in a continuous operation. The pH in the anaerobic region is preferably maintained in the range of 10.5 to 6.5, more preferably in the range of 9.5 to 6.5, and most preferably in the range of 9.0 to 7.5. By controlling the pH drop in such a way that the pH is maintained within those ranges, the drop in the rate of oxidation reaction at the anode can be inhibited. It is also to be noted that many of the enzymes possessed by microorganisms have optimum pHs near neutrality and too strong an alkalinity may inhibit a reduction reaction of the microorganisms. The alkaline substance that can be used in the present invention to effect pH control in the anaerobic region of the biological power generator may be any substance that shows alkalinity in aqueous solution and preferred examples include alkali metals, alkaline earth metals, as well as hydroxides thereof, salts consisting of a strong base and a weak acid, and ammonia. Also applicable are substances of high alkalinity that show neutral to weakly alkaline pH in aqueous solution but whose aqueous solutions have a buffer action. Preferred examples include borates, phos-

phates, and carbonates. When the substances mentioned above are to be used as alkaline substances, two or more of them may be added simultaneously. In the anaerobic region of the biological power generator, the temperature of the solubilized liquid under treatment is preferably maintained in the range of 10°C to 70°C, preferably in the range of 20°C to 45°C, and most preferably in the range of 25°C to 35°C.

[0049] An apparatus for treating organic solid pollutant-containing waste according to the first aspect of the present invention which relates to the treatment of organic waste comprises:

a solubilizing vessel in which the organic solid pollutants in the organic solid pollutant-containing waste are solubilized to form a solubilized liquid under treatment which contains solubilized organic substances; and

a biological power generator comprising an anaerobic region that is furnished with a liquid-under-treatment receiving inlet for receiving the solubilized liquid under treatment and which contains microorganisms capable of growth under anaerobic conditions and an anode having an electron mediator immobilized thereon and having a standard electrode potential (E_0') in the range of -0.13 V to -0.28 V at pH 7, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region.

[0050] The solubilizing vessel may be provided with a mechanical crushing apparatus such as a mill or a stone mortar, an apparatus such as a sonicator, a steamer, a blaster, a hydrothermal electrolyzer or a heater, or a container equipped with a mechanism for feeding a chemical substance such as an acid, alkali, ozone, hypochlorous acid or hydrogen peroxide, and an agitator.

[0051] The biological power generator comprises the anaerobic region which contains the electrode-active microorganisms and the anode having an electron mediator immobilized thereon, the aerobic region containing the cathode, and the diaphragm that defines the anaerobic region and the aerobic region. The anode having an electron mediator immobilized thereon is such that the electron mediator is immobilized on an electrode substrate and it has a standard electrode potential (E_0') in the range of -0.13 V to -0.28 V at pH 7. The anaerobic region is provided with an inlet for receiving the solubilized liquid under treatment. Using as the substrate the solubilized organic substances in the solubilized liquid under treatment that has been fed into the anaerobic region, the electrode-active microorganisms in the anaerobic region proceed with the oxidation reaction whereas in the aerobic region, the reduction reaction which uses oxygen as an electron acceptor is allowed to proceed at the cathode. In this way, the biological power generator promotes the oxidation reaction in the biological reaction system to generate electricity.

[0052] If desired, the treatment apparatus of the present invention may be provided with an aerobic microbial treatment vessel that further treats the treated water from the biological power generator. It may also be provided with a mechanism that recovers the excess sludge from the aerobic microbial treatment vessel and returns it to the solubilizing vessel. In this case, part or all of the excess sludge emerging from the aerobic microbial treatment vessel may be returned to the solubilizing step, whereby the difficult-to-decompose organic matter in the excess sludge is solubilized and decomposed as the substrate for the microbial reaction in the anaerobic region in the biological power generator, thus offering the added advantage of reducing the volume of the excess sludge.

[0053] It is also possible to provide other post-treatment facilities that receive the treated water from the biological power generator, as exemplified by such treatment facilities as for flocculation and precipitation, filtering through activated carbon, phosphate removal, denitrification, and sulfate reduction.

[0054] If desired, a polymer-degradation vessel for further treating the organic substances in the solubilized liquid under treatment to have a smaller molecular weight may be provided between the solubilizing vessel and the biological power generator.

<Treatment for Rendering the Organic polymeric substance-containing Liquid Waste to Have Smaller Molecular Weight>

[0055] The second aspect of the present invention for treating organic waste is characterized by rendering organic polymeric substances to have a smaller molecular weight before feeding the waste into the biological power generator. Specifically, it provides a method of treating organic polymeric substance-containing wastewater by making use of a biological power generator comprising an anaerobic region containing electrode-active microorganisms and an anode having an electron mediator immobilized thereon and having a standard electrode potential (E_0') in the range of -0.13 V to -0.28 V at pH 7, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region, characterized by comprising: a polymer-degradation step in which the organic polymeric substances in the organic polymeric substance-containing liquid waste are reduced in molecular weight to form a liquid under treatment of a smaller molecular weight, and which contains organic substances reduced in molecular weight; and a biological power generation step in which the liquid of smaller molecular weight under treatment is fed into the anaerobic region of the biological power generator so that the oxidation reaction by the microorganisms which use the organic substances reduced in molecular weight within the anaerobic region as an electron donor and the reduction reaction which uses the oxygen within the aerobic region as an electron acceptor are allowed to proceed to

thereby reduce the pollution load in the liquid of smaller molecular weight under treatment while generating electricity.

[0056] The organic polymeric substance-containing liquid waste is not limited in any particular way as long as it is liquid waste that contains polymeric substances such as soluble proteins, polysaccharides, etc. and examples include wastewater from food processing plants, night soil, etc. In addition, even wastewater containing organic solid waste as exemplified by residues from food processing such as coffee grounds, waste brewer's yeast, and bean curd refuse, as well as leftover food (garbage), waste paper, animal waste, and excess sludge can be treated if the solid waste have been reduced in size to such an extent that they will not prevent the anode from contacting the anaerobic microorganisms within the anaerobic region or if they are soluble.

[0057] In the polymer-degradation step, the organic polymeric substances contained in the organic polymeric substance-containing liquid waste, as exemplified by proteins, cellulose, polysaccharides, triglycerides, and higher fatty acids, are preferably reduced in molecular weight by a biological treatment that utilizes the metabolic reaction of anaerobic microorganisms or an enzymatic treatment that utilizes the decomposing reaction by enzymes. The anaerobic microorganisms that can be utilized in the biological treatment may be any anaerobic microorganisms that have the ability to degrade organic polymeric substances (and which are called "organic polymer degrading anaerobic microorganisms") and preferred examples include Clostridium thermocellum, Closdridium stercorarium, Cellulomonas josui, Thermotoga neapolitana, Thermoanaerobacter wiegelii, Coprothermobacter proteolyticus, Coprothermobacter platensis, Caloramator proteoclasticus, Caloramator coolhaasii st. Z, as well as those which produce VFA (volatile fatty acids) from their intermediates, as exemplified by the genera Acetivibrio, Bacteroides, Ruminococcus, Lactobacillus, Sporolactobacillus, Streptococcus, and Biffidobacterium. From a practical viewpoint, an enriched culture of acid fermenting bacteria that are contained in the sludge within the acid fermenting vessel in a two-phase methane generator can preferably be used.

[0058] Preferred examples of enzymes that can be used in the enzymatic treatment include cellulase which is a cellulose decomposing enzyme, protease which is a protein decomposing enzyme, and lipase which is a triglyceride decomposing enzyme.

[0059] The rendering of the organic polymeric substances to have a smaller molecular weight by the biological or enzymatic treatment does not require expensive chemicals but have only to provide a simple reaction vessel (polymer-degradation vessel) in the biological power generator, thus offering an added advantage of lowering the equipment cost as well as the costs for maintenance and management.

[0060] Before it is fed into the anaerobic region of the biological power generator, the organic polymeric substance-containing liquid waste becomes a liquid under treatment of a smaller molecular weight under, and which contains organic substances that have been reduced in molecular weight by the above-described polymer-degradation step. The organic substances that have been reduced in molecular weight are preferably such that monosaccharides and volatile fatty acids that can be readily oxidized by the electrode-active microorganisms are contained as main ingredients; more preferably, they contain small amounts of monosaccharides and volatile fatty acids as the main ingredient; and it is particularly preferred that the carbon source for the electrode-active microorganisms consists essentially of volatile fatty acids. If saccharides occur at high concentrations in the liquid of smaller molecular weight under treatment, acid fermenting microorganisms which produce extracellular polymers of high viscosity will become dominant and the extracellular polymers may sometimes adhere to the anode's surface, undesirably preventing the anode from contacting the electrode-active microorganisms. Another advantage of limiting the carbon source for the electrode-active microorganism to volatile fatty acids is that microorganisms other than the electrode-active microorganisms, for example, those which decompose the organic polymeric substances by a moderate degree to produce intermediate metabolites (e.g., Clostridium thermocellum, Closdridium stercorarium, Cellulomonas josui, Thermotoga neapolitana, Thermoanaerobacter wiegelii, Coprothermobacter proteolyticus, Coprothermobacter platensis, Caloramator proteoclasticus, Caloramator coolhaasii st. Z), as well as those which decompose the intermediate metabolites (e.g., saccharides) to produce volatile fatty acids (e.g., the genera Acetivibrio, Bacteroides, Ruminococcus, Lactobacillus, Sporolactobacillus, Streptococcus, and Biffidobacterium) are suppressed in proliferation to provide ease for the electrode-active microorganisms to become dominant. Volatile fatty acids that can be fed as the substrate for the electrode-active microorganisms are preferably those volatile fatty acids having no more than six carbon atoms which can be readily oxidized by the anaerobic microorganisms in the anaerobic region and examples include formic acid, acetic acid, propionic acid, butyric acid, valeric acid, isovaleric acid, lactic acid, succinic acid, and caproic acid.

[0061] In the polymer-degradation step, the pH of the organic polymeric substance-containing liquid waste is preferably controlled to lie in the range of 4.0 to 6.5, especially in the range of 4.5 to 5.5. As the organic polymer decomposing anaerobic microorganisms proceed with acid fermentation using the organic polymeric substances as the substrate, the pH of the liquid of smaller molecular weight under treatment will decrease. If the pH of the organic polymeric substance-containing liquid waste decreases to 4.0 or less, the organic polymer decomposing anaerobic microorganism finds difficulty proceeding with the acid fermentation reaction (reaction for producing volatile fatty acids); under conditions close to neutrality (pH 7), there is high likelihood for the occurrence of mixed acid fermentation which produces acetic acid and various other organic acids and, depending on the type of the substrate used, hydrogen gas may evolve and escape from the liquid phase in the process of realizing a smaller molecular weight. Allowing hydrogen gas to evolve is

undesirable not only from the viewpoint of safety management but also from the viewpoint of efficient energy recovery.

[0062] If wastewater with high concentrations of organic polymers is supplied, the organic polymers are rapidly reduced in molecular weight and the pH of the liquid of smaller molecular weight under treatment will decrease rapidly. Suppose here that a low-pH liquid of smaller molecular weight under treatment is fed into the anaerobic region of the biological power generator. Since the rate-limiting factor to the overall reaction rate in the method of biological power generation is the oxidation reaction at the anode, the pH of the solution in the anaerobic region of the biological power generator will drop sharply, directly leading to a drop in the quantity of electricity generated. Since the metabolic reaction in the electrode-active microorganisms is an enzymatic reaction, it has a buffering capability against a certain amount of changes in the concentration of hydrogen ion. On the other hand, the oxidation reaction at the anode is a chemical reaction and determined by the concentration of electron mediator and that of hydrogen ion, as expressed by the following equation (1).

[Chemical Formula 1]

$$Mediator_{Red} \leftrightarrow Mediator_{Ox} + e^- + H^+ \qquad \text{Eq. (1)}$$

[0063] (where $Mediator_{Red}$ represents a reduced redox substance, $Mediator_{0x}$ represents an oxidized redox substance, e^- represents an electron, and H^+ represents a hydrogen ion.)
The equilibrium constant K for the process is expressed by the following equation (2).

[Chemical Formula 2]

$$k = \frac{[\text{MediatorOx}][\text{H+}]}{[\text{MediatorRed}]} \qquad \text{Eq. (2)}$$

[0064] The electron emitted in the above Eq. (1) is discharged from the anode to the outside of the system, so the concentration of hydrogen ions is a factor that largely contributes to the reaction at the anode. According to this principle, the higher the concentration of hydrogen ions, the lower the concentration of the oxidized form of redox substance; as a result, the reaction will readily reach an equilibrium and no more electric current will flow. Hence, it is desirable that the concentration of hydrogen ions in the liquid of smaller molecular weight under treatment to be fed into the biological power generator is not excessively high. In the present invention, if the pH is appropriately controlled in the step of reducing the molecular weight of the organic polymeric substances in the liquid under treatment, there is offered another advantage of providing ease in controlling the pH in the anaerobic region of the biological power generator into which is fed the liquid under treatment that has passed through the polymer-degradation step.

[0065] Controlling the pH of the organic polymeric substance-containing liquid waste is preferably carried out by recovering an alkaline solution from the aerobic region of the biological power generator and feeding the recovered alkaline solution into the anaerobic region. This mode has the advantage of cutting the cost of the alkali agent. However, this is not the sole case of the present invention and an alkaline substance may separately be added in the polymer-degradation step. The alkaline substance that can be used for pH control may be any substance that shows alkalinity in aqueous solution and preferred examples include alkali metals, alkaline earth metals, as well as hydroxides thereof, salts consisting of a strong base and a weak acid, and ammonia. Also applicable are substances of high alkalinity that show neutral to weakly alkaline pH in aqueous solution but whose aqueous solutions have a buffer action. Preferred examples include borates, phosphates, and carbonates. When the substances mentioned above are to be used as alkaline substances, two or more of them may be added simultaneously.

[0066] As in its first aspect, the present invention according to the second aspect which relates to the treatment of organic waste may be so adapted that the treated water from the biological power generator is subjected to a post-treatment such as flocculation and precipitation, filtering through activated carbon, phosphate removal, denitrification or sulfate reduction. If liquid waste containing organic solid pollutants such as sludge is used as the organic polymeric substance-containing liquid waste, it is preferably subjected to the polymer-degradation step after the solids are reduced to fine particles by mechanical or physical crushing or their solubility is enhanced by chemical reaction.

[0067] In the second aspect of the present invention for the treatment of organic waste, the liquid of smaller molecular weight under treatment is then subjected to the biological power generation step. In the biological power generation step, the oxidation reaction of the microorganisms which use as an electron donor the organic substances that have been reduced in molecular weight in the liquid of smaller molecular weight under treatment that has been fed into the anaerobic region of the biological power generator and the reduction reaction which uses the oxygen in the aerobic region as an electron acceptor are allowed to proceed to thereby reduce the pollution load in the liquid of smaller molecular weight under treatment while generating electricity. In the biological power generation step, the liquid of smaller molecular weight under treatment is controlled under conditions that can maintain the activity of the electrode-active microorganisms occurring in the anaerobic region. For example, by controlling the drop of the pH of the liquid of smaller molecular weight under treatment within the anaerobic region, the reduced mediator at the anode can be prevented from suffering a drop in the rate of oxidation reaction and a large current density can be obtained even in a continuous operation. The pH in the anaerobic region is preferably maintained in the range of 10.5 to 6.5, more preferably in the range of 9.5 to 6.5, and most preferably in the range of 9.0 to 7.5. By controlling the pH drop in such a way that the pH is maintained within those ranges, the drop in the rate of oxidation reaction at the anode can be inhibited. It is also to be noted that many of the enzymes possessed by microorganisms have optimum pHs near neutrality, and too strong an alkalinity may inhibit a reduction reaction of the microorganisms. The alkaline substance that can be used in the present invention to effect pH control in the anaerobic region of the biological power generator may be any substance that shows alkalinity in aqueous solution, and preferred examples include alkali metals, alkaline earth metals, as well as hydroxides thereof, salts consisting of a strong base and a weak acid, and ammonia. Also applicable are substances of high alkalinity that show a neutral to weakly alkaline pH in aqueous solution but whose aqueous solutions have a buffer action. Preferred examples include borates, phosphates, and carbonates. When the substances mentioned above are to be used as alkaline substances, two or more of them may be added simultaneously. A temperature of the liquid of a smaller molecular weight under treatment is maintained in the range of 20°C to 70°C, and preferably in the range of 30°C to 70°C.

[0068] An apparatus for treating organic polymeric substance containing liquid waste according to the second aspect of the present invention which relates to the treatment of organic waste comprises:

a polymer-degradation vessel in which organic polymeric substances in organic polymeric substance-containing liquid waste are reduced in molecular weight to form under treatment a liquid of a smaller molecular weight, and which contains organic substances that have been reduced in molecular weight; and

a biological power generator comprising an anaerobic region that is furnished with a receiving inlet for receiving the liquid under treatment of the smaller molecular weight, and which contains microorganisms capable of growth under anaerobic conditions and an anode having an electron mediator immobilized thereon, and having a standard electrode potential (E_0') in the range of -0.13 V to -0.28 V at pH 7, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region.

[0069] The polymer-degradation vessel is not particularly limited in shape and size as long as it is a vessel comprising an inlet for receiving the organic polymeric substance-containing liquid waste, an outlet for discharging the liquid under treatment of the smaller molecular weight, which contains the organic substances that have been reduced in molecular weight, and an optional pH control mechanism for controlling the pH of the fluid being treated for reduction in molecular weight. A preferred pH control mechanism is one that comprises an alkaline solution recovery vessel, which will be described later, that recovers an alkaline solution from the aerobic region of the biological power generator and an alkaline solution supply mechanism for feeding the recovered alkaline solution into the polymer-degradation vessel. Use of this pH control mechanism is particularly advantageous since it is possible to cut not only a required amount of the pH adjusting chemical but also emission of the alkaline solution from the aerobic region of the biological power generator.

[0070] The biological power generator comprises the anaerobic region which contains the electrode-active microorganisms, and the anode having an electron mediator immobilized thereon, the aerobic region containing the cathode, and the diaphragm that defines the anaerobic region and the aerobic region. The anode having an electron mediator immobilized thereon is such that the electron mediator is immobilized on an electrode substrate and has a standard electrode potential (E_0') in the range of -0.13 V to -0.28 V at pH 7. The anaerobic region is provided with an inlet for receiving the liquid under treatment of the smaller molecular weight. Using as the substrate the organic substances that have been reduced in molecular weight in the liquid under treatment of smaller molecular weight that has been fed into the anaerobic region, the electrode-active microorganisms in the anaerobic region proceed with the oxidation reaction, whereas in the aerobic region, the reduction reaction which uses oxygen as an electron acceptor is allowed to proceed at the cathode. In this way, the biological power generator promotes the oxidation reaction in the biological reaction system to thereby generate electricity.

[0071] It is preferred that the biological power generator further includes a mechanism that controls the pH of the liquid under treatment of smaller molecular weight within the anaerobic region. An applicable pH control mechanism is a common pH control mechanism comprising a pH meter for measuring the pH of the liquid under treatment of smaller

molecular weight, a control mechanism for controlling the supply of an alkaline chemical based on the result of measurement with the pH meter, and an alkaline chemical reservoir for holding the alkaline chemical.

[0072] If desired, the treating apparatus according to the second aspect of the present invention may include post-treatment equipment for receiving the treated water from the biological power generator, as exemplified by a flocculation and precipitation vessel, an activated carbon assisted filtering vessel, a dephosphorylation vessel, a denitrification vessel, or a sulfate reduction vessel. If liquid waste containing organic solid pollutants such as sludge is used as the organic polymeric substance-containing liquid waste in the treating apparatus of the present invention, a device for reducing solids to fine particles, or for improving solubility, as exemplified by a mechanical crusher (e.g., a stone mortar or a mill), a sonicator, a hydrothermal electrolyzer, or a chemical reaction vessel, is preferably provided between the raw water reservoir and the polymer-degradation vessel.

<Post-treatment>

[0073] The third aspect of the present invention which relates to the treatment of organic waste is characterized by including a post-treatment in which the primary treated water as obtained by primary treatment with the biological power generator is further treated.

[0074] According to the third aspect of the present invention, there is provided a method of treating organic solid pollutant-containing wastewater by making use of a biological power generator comprising an anaerobic region containing microorganisms capable of growth under anaerobic conditions, and an anode having an electron mediator immobilized thereon and having a standard electrode potential (E_0') in the range of -0.13 V to -0.28 V at pH 7, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region, the method comprising: a biological power generation step in which organic pollutant-containing liquid waste is fed into the anaerobic region of the biological power generator so that the oxidation reaction by the microorganisms which use organic pollutants within the anaerobic region as an electron donor, and the reduction reaction which uses the oxygen within the aerobic region as an electron acceptor are allowed to proceed to thereby reduce a pollution load in the organic pollutant-containing liquid waste while generating electricity; and a post-treatment step in which the pollution load in the treated water as obtained by the biological power generation step is further reduced.

[0075] The organic pollutant-containing liquid waste may be any fluid such as liquids, dispersions, suspensions or slurries that contain biodegradable substances, and it may be exemplified by wastewater from food processing plants, night soil, and the like. In addition, organic solid waste as exemplified by residues from food processing such as coffee grounds, waste brewer's yeast, and bean curd refuse, as well as leftover food (garbage), waste paper, animal waste, and excess sludge may be mechanically crushed on a mill or a stone mortar or by sonication, chemically treated with acid, alkali or ozone, or treated by heat or otherwise so that they are dispersed or suspended as fine particles and/or converted to soluble substances, whereupon they assume a state in which they cannot be easily separated from the liquid under treatment; such liquid waste can also be treated. The organic pollutant-containing liquid waste can also be treated after it is preliminarily subjected to a biological treatment to reduce the molecular weight of the pollutants.

[0076] The treatment method under consideration comprises two steps, the first for treating the organic pollutants in the biological power generator and the subsequent post-treatment of the treated liquid. First there will be described the biological power generation step which makes use of the biological power generator.

[0077] In the treatment method under consideration, the organic pollutant-containing liquid waste is first fed into the biological power generator comprising an anaerobic region that contains microorganisms capable of growth under anaerobic conditions, and an anode having an electron mediator immobilized thereon and having a standard electrode potential (E_0') in the range of -0.13 V to -0.28 V at pH 7, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region, and the organic pollutants in the liquid waste undergo the decomposing action of the anaerobic microorganisms in the anaerobic region, whereupon they are converted to substances of a smaller pollution load. An index preferably used to evaluate the pollution load is at least one member of the group consisting of BOD (biochemical oxygen demand), COD (chemical oxygen demand), nitrogen concentration, and phosphorus concentration, with BOD being particularly preferred.

[0078] The biological power generator comprises the anaerobic region which contains the microorganisms capable of growth under anaerobic conditions and the anode having an electron mediator immobilized thereon, the aerobic region containing the cathode, and the diaphragm that defines the anaerobic region and the aerobic region to allow for fluid communication. The anode having the electron mediator immobilized thereon is such that the electron mediator is immobilized on an electrode substrate and it has a standard electrode potential (E_0') in the range of -0.13 V to -0.28 V at pH 7. The anaerobic region is provided with a feed inlet through which the organic pollutant-containing liquid waste is fed. Using as the substrate the organic pollutants in the organic pollutant-containing liquid waste that has been fed into the anaerobic region, the anaerobic microorganisms in the anaerobic region proceed with the oxidation reaction whereas in the aerobic region, the reduction reaction which uses oxygen as an electron acceptor is allowed to proceed at the cathode. In this way, the oxidation reaction in the biological reaction system is promoted to generate electricity

while, at the same time, the organic substance-containing waste is cleaned by the anaerobic microorganisms. There may be further included the solubilizing treatment and/or the polymer-degradation step that have been explained in connection with the first and second aspects of the present invention which relates to the treatment of organic waste.

[0079] We next explain the post-treatment step.

[0080] The post-treatment step is preferably at least one member of the group consisting of a flocculation and precipitation step, a filtering step through activated carbon, a decomposition treatment step by means of aerobic microorganisms, a decomposition treatment step by means of anaerobic microorganisms, a denitrification step, a phosphate removal step, an acid decomposing step, and an oxidation and reduction treatment step by means of electrode-active microorganisms; particularly preferred is an oxidation and reduction treatment step by means of electrode-active microorganisms, in which the treated water from the biological power generator is fed into the anaerobic region and both the oxidation reaction of microorganisms that use the organic pollutants in the anaerobic region as an electron donor and the reduction reaction that uses the oxygen in the aerobic region as an electron acceptor are allowed to proceed, thereby reducing the pollution load in the organic pollutant-containing liquid waste.

[0081] An applicable flocculation and precipitation step is one that involves the addition of a flocculant such as aluminum sulfate or polyacrylamide. The decomposition treatment step by means of aerobic microorganisms can be performed by aeration, distribution over a trickling filter, or the like; the decomposition treatment step by means of anaerobic microorganisms can utilize methanogenesis or the like. For the denitrification step, a nitrogen removing apparatus may be used that is furnished with a denitrification vessel and a nitrification vessel. For the phosphate removal step, one may typically use a phosphate removing apparatus furnished with an anaerobic vessel and an aerobic vessel, or a phosphorus removing apparatus loaded with phosphate rock; alternatively, one may add magnesium chloride and an alkali. For the oxidative decomposing step, one may use ozone, hydrogen peroxide, potassium permanganate, hydroxy radicals from the Fenton reaction, UV irradiation, and the like.

[0082] A post-treatment step that is particularly preferred for the present invention is an oxidation and reduction treatment step by means of electrode-active microorganisms, in which both the oxidization reaction of the microorganisms that use the organic pollutants in the anaerobic region as an electron donor and the reduction reaction that uses the oxygen in the aerobic region as an electron acceptor are allowed to proceed, thereby reducing the pollution load in the organic pollutant-containing liquid waste. The oxidation and reduction treatment step by means of electrode-active microorganisms is preferably performed using the second biological power generator which may be composed in basically the same way as the biological power generator. Using the biological power generator in the post-treatment step is advantageous in that there is no need to use mechanical power for aeration, nor does exist the need for chemicals such as flocculants or activated carbon.

[0083] If the second biological power generator is used in the post-treatment step, the anode in it preferably has a higher standard electrode potential (E_0') than the anode in the biological power generator employed in the biological power generation step. By using an anode having a higher standard electrode potential than in the biological power generator employed in the biological power generation step, it becomes easy to remove the organic pollutants to such an extent that the BOD level reaches the low concentration that has been unable to attain by removal in the biological power generation step. In order to make anodes having different standard electrode potentials, one may immobilize different kinds of electron mediator on the anode. Specifically, this can be achieved by ensuring that an electron mediator to be immobilized on the anode in the second biological power generator has a higher standard electrode potential (E_0') than the electron mediator immobilized on the anode in the biological power generator employed in the biological power generation step, for example, a standard electrode potential (E_0') higher than -0.13 V.

[0084] The electron mediator that can be immobilized on the anode in the second biological power generator is preferably exemplified by at least one member of the group consisting of anthraquinone derivatives, naphthoquinone derivatives, benzoquinone derivatives, isoalloxazine derivatives, ubiquinone derivatives, cytochrome derivatives, and iron-rich smectite derivatives. Specifically, at least one member is preferably mentioned, as selected from the group consisting of anthraquinone carboxylic acids (AQC), aminoanthraquinones (AAQ), diaminoanthraquinones (DAAQ), anthraquinone sulfonic acids (AQS), diaminoanthraquinone sulfonic acids (DAAQS), anthraquinone disulfonic acids (AQDS), diaminoanthraquinone disulfonic acids (DAAQ DS), ethyl anthraquinones (EAQ), methyl naphtoquinones (MNQ), methyl aminonaphtoquinones (MANQ), bromomethyl aminonaphtoquinones (BrMANQ), dimethyl naphtoquinones (DMNQ), dimethyl aminonaphtoquinones (DMANQ), lapachol (LpQ), hydroxy(methylbutenyl)aminonaphthoquinones (AlpQ), naphthoquinone sulfonic acids (NQS), trimethyl aminobenzoquinones (TMABQ), flavin mononucleotide (FMN), ubiquinone (UQ), 1,4-benzoquinone (1,4-BQ), cytochrome *a*, cytrochrome *b*, cytochrome *c*, nontronite, and derivatives thereof.

[0085] To immobilize these electron mediators on the anode, the chemical bonding methods shown in Tables 3 and 4 may be adopted as in the case of immobilization on the anode in the biological power generator employed in the biological power generation step if they are quinone-containing substances such as anthraquinone derivatives, naphthoquinone derivatives, benzoquinone derivatives, isoalloxazine derivatives, and ubiquinone derivatives.

[0086] A method of immobilizing cytochrome or its derivatives as the electron mediator on the electrode substrate is

such that N-succimidyl-3-maleimidopropionic acid is dehydratively condensed on an amino group that has been introduced into an electrically conductive substrate for anode and the thiol group in the cysteine residue of cytochrome is attached nucleophilically to the condensation product for bonding. Specifically, if graphite is used as the electrically conductive substrate, sulfanilic acid and a nitrite are first allowed to act on the graphite to introduce a sulfonic acid group by the diazo coupling reaction. This is then reacted with oxalyl chloride to form sulfonyl chloride, on which a diamine such as 1,3-propandiamine is allowed to act in the solvent THF, thereby introducing an amino group. An equimolar or greater amount of N-succimidyl-3-maleimidopropionic acid is added with respect to the introduced amino group and allowed to react in the presence of dicyclohexyl carbodiimide, whereby an amide bond is formed between the carboxyl group in the N-succimidyl-3-maleimidopropionic acid and the amino group on the graphite to make a monomolecular layer of maleimide. An equimolar or greater amount of cytochrome is added with respect to the immobilized maleimide and the thiol group in the cysteine residue of the cytochrome is nucleophilically attached to the maleimide, whereby the cytochrome can be finally immobilized on the graphite's surface. An applicable method of immobilizing iron-rich smectite comprises crushing it with a ball mill or the like, suspending the particles in either a Nafion (registered trademark of DuPont)/isopropanol solution or a polyacrylic acid/methanol solution, mixing the suspension with a carbon black powder, and applying the mixture to a porous graphite sheet or the like.

[0087] The cathode, the diaphragm, and the electrode-active microorganisms in the second biological power generator that can be used in the post-treatment step may have the same constructions as the cathode, the diaphragm and the electrode-active microorganisms in the biological power generator that is utilized in the biological power generation step. It should, however, be noted that the anode-cathode circuit to be installed in the second power generator need not have any power utilizing device connected therebetween but that a conductor wire is preferably used to form a circuit without load or with only an extremely small load being inserted. By forming a circuit without load or with only an extremely small load being inserted, even the electron mediator having a comparatively high standard electrode potential (E_0') that is to be installed in the second power generator can be efficiently oxidized at the anode.

[0088] Thus, according to the third aspect of the present invention, there is provided an apparatus for treating organic pollutant-containing wastewater that comprises a biological power generator comprising an anaerobic region containing microorganisms capable of growth under anaerobic conditions and an anode having an electron mediator immobilized thereon and having a standard electrode potential (E_0') in the range of -0.13 V to -0.28 V at pH 7, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region; and a post-treatment vessel for further reducing the pollution load in the treated water from the biological power generator.

[0089] The post-treatment vessel is preferably at least one member of the group consisting of a flocculation and precipitation vessel, an activated carbon assisted filtering vessel, a vessel for decomposition treatment by aerobic microorganisms, a vessel for decomposition treatment by anaerobic microorganisms, a denitrification vessel, a dephosphorylation vessel, an acid decomposing vessel, and a biological power generating vessel.

EFFECTS OF THE INVENTION

[0090] According to the first aspect of the present invention for the treatment of organic waste, organic solid pollutant-containing waste such as wastewater, liquid waste, night soil, food waste, and sludge that are to be fed into the biological power generator are preliminarily solubilized so that the efficiency of the oxidation-reduction reaction in the biological power generator is ensured to draw electrical energy while purifying the organic solid pollutant-containing waste in a simple and efficient way. If excess sludge from an aerobic microbial treatment vessel in water treatment facilities is used as the organic solid pollutant-containing waste, the present invention also contributes to reducing the volume of excess sludge containing large amounts of difficult-to-decompose organic matter.

[0091] In addition, according to the second aspect of the present invention for the treatment of organic waste, organic polymeric substance-containing wastewater such as wastewater, liquid waste, night soil, food waste, and sludge that are to be fed into the biological power generator are preliminarily treated for reduction in molecular weight so that the efficiency of the oxidation-reduction reaction in the biological power generator is ensured to draw electrical energy while purifying the organic polymeric substance-containing wastewater in a simple and efficient way.

[0092] Furthermore, according to the third aspect of the present invention for the treatment of organic waste, two conflicting demands, an improved efficiency of water treatment and increased power generation, can be met at the same time. Take, for example, the case where liquid waste containing such substances as cellulose that are biologically decomposed at a comparatively slow rate is continuously treated; with the biological power generator used alone, the reaction for oxidation of the organic matter by microorganisms in the anaerobic region proceeds and the BOD decreases. In particular, at the point in time when the BOD has dropped below 1000 mg/L, a phenomenon is observed such that the oxidation-reduction potential (ORP) in the anaerobic region gradually rises (changes to an oxidative state) while at the same time, less electricity is generated. As the result, the rate of BOD removal decreases, making it difficult to remove the BOD to a sufficiently low concentration. In short, under low BOD conditions, the amount of power generation decreases while at the same time, the rate of the BOD load consumption in the anaerobic region decreases. To unravel

the cause of this phenomenon, the present inventors made intensive studies and have obtained the following observation. When the BOD in the anaerobic region decreases, the supply of the reducing power from the organic matter to microorganisms decreases and so does the concentration of reduced nicotinamide adenine dinucleotide (NADH) which is a reducing substance in the bodies of microorganisms. Then, the concentration of the terminal reductase or the extracellular released electron mediator (such as menaquinone derivatives), whichever is in the reduced form, also decreases. In this state, the frequency at which the electron mediator immobilized on the anode is reduced also decreases. Then, on account of the rate limiting of the reduction reaction on the part of the microorganisms, the rate of supply of the reduced electron mediator decreases and so does the amount of an electric current that is produced by the anode which is oxidizing the mediator. Particularly in the case where a substance having a low standard electrode potential (E_0') is used as the anode having an electron mediator immobilized thereon, the BOD decreases to afford a lowered reducing power and if the oxidation-reduction potential (ORP) in the anaerobic region rises to a level beyond the oxidation-reduction potential of the anode having an electron mediator immobilized thereon, the electron mediator can no longer exist in the reduced form, with the result that virtually no electric current will flow.

[0093] On the other hand, however, in order to obtain the largest possible quantity of electricity from the biological power generator, the potential difference between anode and cathode must be increased and, to this end, the anode having an electron mediator immobilized thereon desirably has a standard electrode potential that is within the range of -0.13 V to -0.28 V but which is as close as possible to -0.28 V. Consequently, there exist two conflicting demands: in order to lower the BOD concentration in the treated water, the anode having an electron mediator immobilized thereon should have the highest possible standard electrode potential, but in order to ensure that the power generator will generate a large quantity of electricity, the anode having an electron mediator immobilized thereon desirably have the lowest possible standard electrode potential.

[0094] The treatment method and apparatus according to the third aspect of the present invention are characterized in that an anode having an electron mediator immobilized thereon and which has a low standard electrode potential is employed in the biological power generation step or within the biological power generator so as to secure a high level of power generation whereas an anode having an electron mediator immobilized thereon and which has a high standard electrode potential is employed in the post-treatment step or within the second biological power generator so as to secure a high BOD decomposing ability, with the result that both treated water of good quality and high power generating capability can be realized simultaneously.

[0095] A method of treating organic substances using only the biological power generator has the feature that compared to the biological treatment using aerobic microorganisms such as the activated sludge method, a smaller amount of sludge is produced, so excess sludge can be disposed of at a lower cost. On the other hand, however, due to the small quantity of the excess sludge produced, smaller amounts of nitrogen and phosphorus will be incorporated into the excess sludge, occasionally causing higher concentrations of nitrogen and phosphorus to leak into the treated water. According to the treatment methods and apparatuses of the present invention, the treated water from the biological power generation apparatus may be treated in the post-treatment step or in the post-treatment vessel, whereby the treated water can be deprived of nitrogen and phosphorus.

[0096] As described above, according to the present invention, a simple apparatus is capable of efficient treatment of waste- water containing organic pollutants such as sludge, wastewater, night soil, food waste, and sludge while producing electrical energy; what is more, treated water with a biological oxygen demand (BOD) of less than 120 mg/L which is the uniform standard for emission (daily average) specified by the Water Pollution Prevention Law can be obtained consistently.

BRIEF DESCRIPTIONS OF THE DRAWINGS

[0097]

[FIG. 1] FIG. 1 is a flow chart depicting a mode of embodiment for the construction of a solid pollutant-containing waste treating apparatus according to the first aspect of the present invention which relates to the treatment of organic waste.

[FIG. 2] FIG. 2 is a conceptual diagram showing the basic construction of the biological power generator of the present invention.

[FIG. 3] FIG. 3 is a diagram showing in concept a biological power generator which is a unitary assembly of the biological power generator shown in FIG. 2.

[FIG. 4] FIG. 4 shows in section an example of the cathode structure in the biological power generator.

[FIG. 5] FIG. 5 is a flow chart depicting another mode of embodiment for the construction of the organic solid pollutant-containing waste treating apparatus according to the first aspect of the present invention.

[FIG. 6] FIG. 6 is a flow chart depicting another mode of embodiment for the construction of the organic solid pollutant-containing waste treating apparatus according to the first aspect of the present invention.

[FIG. 7] FIG. 7 shows in concept the experimental biological power generator used in the Examples.
[FIG. 8] FIG. 8 is a flow chart depicting a mode of embodiment for the construction of an organic polymeric substance-containing liquid waste treating apparatus according to the second aspect of the present invention which relates to the treatment of organic waste.
[FIG. 9] FIG. 9 is a flow chart depicting another mode of embodiment for the construction of the organic polymeric substance-containing liquid waste treating apparatus according to the second aspect of the present invention.
[FIG. 10] FIG. 10 is a structural conceptual diagram showing a mode of embodiment for an organic pollutant-containing liquid waste treating apparatus according to the third aspect of the present invention which relates to the treatment of organic waste.
[FIG. 11] FIG. 11 is a structural conceptual diagram showing another mode of embodiment for the organic pollutant-containing liquid waste treating apparatus according to the third aspect of the present invention.
[FIG. 12] FIG. 12 is a structural conceptual diagram showing yet another mode of embodiment for the organic pollutant-containing liquid waste treating apparatus according to the third aspect of the present invention.
[FIG. 13] FIG. 13 is a pair of graphs showing the results of measurement in Example 3.

LEGEND

[0098]

1 Organic solid pollutant-containing waste
2 Raw water reservoir
3 Solubilizing vessel
4 Liquid-under-treatment supply piping
5 Biological power generator

5a Anaerobic region
5b Aerobic region
5c Diaphragm

6 Treated water
7 pH adjusting chemical solution reservoir
8, 8a pH controller
10 Alkali solution recovery vessel
11 Secondary treated water
12 Aeration vessel
13 Precipitation vessel
51 Anode (electrode substrate having an electron mediator immobilized thereon)
52 Diaphragm
53 Cathode
53a Catalyst supporting carbon paper

53b Collector

54 Anaerobic region (microorganism compartment)
55 Aerobic region (air compartment)
64 Air intake port
66 Condensed water drain
103 Polymer-degradation vessel
104 Liquid under treatment of a smaller molecular weight (organic substance of smaller molecular weight) supply piping
63 Excess sludge discharge port
65 Exhaust vent
310 Post-treatment vessel
410 Second power generator

MODES OF EMBODIMENT OF THE INVNTION

[0099] On the following pages, various modes of embodiment of the present invention are described in detail with

reference to the accompanying drawings but it should be understood that the present invention is in no way limited to those modes.

<Solubilizing treatment>

[0100] FIG. 1 is a flow chart of an organic solid pollutant-containing waste treating apparatus according to the first aspect of the present invention which relates to the treatment of organic waste. In FIG. 1, the treatment apparatus of the present invention comprises a solubilizing vessel 3 and a biological power generator 5 equipped with an anaerobic region 5a and an aerobic region 5b that are defined by a diaphragm 5c. Connected between the solubilizing vessel 3 and the biological power generator 5 are piping 4 and a pump for feeding a solubilized liquid under treatment to the biological power generator 5. Connected to the anaerobic region 5a of the biological power generator 5 are piping from a pH adjusting chemical reservoir 7 and piping from a pH controller 8. A raw water reservoir 2 for holding organic solid pollutant-containing waste 1 is connected to the solubilizing vessel 3 via piping and a pump. The solubilizing vessel 3 may be a mechanical crushing apparatus such as a mill or a stone mortar, an apparatus such as a sonicator, a steamer, a blaster, a hydrothermal electrolyzer or a heater, or a container equipped with a mechanism for feeding a chemical substance such as an acid, alkali, ozone, hypochlorous acid, or hydrogen peroxide.

[0101] FIG. 2 shows a specific example of the biological power generator 5. For instance, the specific example of the biological power generator illustrated in FIG. 2 is in a three-ply tubular form that consists of an anaerobic region 54 containing an anode for biological power generation 51 with an electron mediator immobilized on it, a diaphragm (electrolyte membrane 52), and an aerobic region 55 containing a porous cathode 53. The anaerobic region 54 which is the innermost spaced spatial form of the tube is preliminarily loaded with a solution or suspension containing electrode-active microorganisms (anaerobic). The anaerobic region 54 is charged with a flow of solubilized liquid under treatment that emerges from the solubilizing vessel 3 as it contains solubilized organic substances (sometimes referred to as a "substrate"). The aerobic region 55 which is the outermost spaced spatial form of the tube is filled with air that contains molecular oxygen. The aerobic region 55 is fitted with a means (not shown) for feeding molecular oxygen. The porous cathode 53 provided within the aerobic region 55 is such that at least part of the cathode is formed of an electrically conductive porous material, net-like or fibrous material that have voids in their structure. The diaphragm 52 separating the anaerobic region 54 and the aerobic region 55 is composed of a diaphragm having a large material exchange coefficient, for example, a solid polymer electrolyte membrane such as Nafion (registered trademark) which is a product of DuPont or NEOSEPTA (registered trademark) manufactured by ASTOM.

[0102] In the anaerobic region 54, microorganisms proceed with an oxidation reaction using solubilized organic substances as an electron donor whereas in the aerobic region 55, a reduction reaction proceeds with oxygen being used as an electron acceptor. In this way, a potential difference occurs between the anode 51 and the cathode 53. As such, the anode 51 and the cathode 53 are connected to a power utilizing device via a conductor wire 56, whereupon a potential difference current flows; at the same time, ions move between the anaerobic region 54 and the aerobic region 55 through the electrolyte membrane 52 to thereby form a closed circuit. As the reaction proceeds, hydrogen ions evolve in the anaerobic region 54, causing the aqueous solution in the anaerobic region 54 to assume acidity. On the other hand, hydroxide ions evolve in the aerobic region 55, causing the water produced within the aerobic region 55 to become an alkaline solution.

[0103] The inside diameter of the tubular element that constitutes a power generating unit may be set at several millimeters to several centimeters, or even several tens of centimeters, depending on the fluidity of the substrate. A power generating unit of the type shown in FIG. 2 may be retained by a support layer or casing of a suitable material so as to increase its physical strength. In this case, the tubular element may in turn be enveloped in an outer shell to form an air compartment in the space between the outer shell and the tubular element, with a means for letting air to flow into and out of the air compartment being formed in the air compartment.

[0104] In the mode of embodiment shown in FIG. 2, the anode 51, diaphragm 52 and the cathode 53 are adapted to have a three-layered cylindrical structure, with the anode 51 and the cathode 53 being separated by the diaphragm 52. This structure contributes to increasing the surface areas of the anode 51 and the cathode 53, as well as ensuring efficient contact between the anode 51 and the substrate so as to minimize the dead zone where the substrate does not move; as a result, efficient ion exchange is assured between the anode 51 and the cathode 53; at the same time, the anode 51 and the cathode 53 are electrically insulated, allowing electrons on the solubilized organic substances (substrate) to be delivered to the anode 51 efficiently. In addition, by causing the porous cathode 53 to contact the air, with a contact interface between the air and water occurring within voids in the cathode 53, the efficiency of contact with the oxygen in the air and the water at the water surface can be increased, whereby the reduction reaction of oxygen on the electrode can be allowed to proceed efficiently.

[0105] Depending on the use, the anode containing anaerobic region of the biological power generator of a three-layered tubular form as shown in FIG. 2 may be positioned outside and the cathode containing aerobic region positioned inside, with an air passage means being provided in the aerobic region and the whole apparatus being installed within

the substrate solution and operated for power generation. If desired, the tubular element may be formed in a particular shape, for instance, a U-shape, with both of its ends protruding from the liquid surface of the substrate solution so that air can flow into the space within the tube. An advantage of this design having the aerobic region formed as the inner tube is that even if the inside diameter of the inner tube formed of the aerobic region is reduced to about several millimeters or less, there is no risk of the occurrence of clogging. The three-layered tubular element may also be adapted such that the inside tubular element provides an aerobic region containing a porous cathode whereas the outside tubular element provides an anaerobic region containing an anode, and this design is advantageous since the outside anode can be made to have a greater surface area than the cathode. The surface area of the anode can be further increased by providing asperities or folds on the anode surface. Regarding the inside diameter across the cathode, which also relates to the reaction efficiency, it may suffice to permit easy passage of air and at least risk for clogging, the inside diameter can be reduced to about several millimeters or less. In this case, the tubular element may in turn be enveloped in an outer shell to form a microbial reaction compartment in the space outside the tubular element through which the substrate can flow, with a means for letting the substrate to flow into and out of the microbial reaction compartment being formed in that compartment.

[0106] If desired, a plurality of biological power generating units in either the tubular form shown in FIG. 2 or in other form may be placed side by side to compose a biological power generator. For example, FIG. 3 shows a mode in which a plurality of the biological power generating units of the type shown in FIG. 2 are placed side by side, and FIG. 7 shows a mode using a biological power generating unit in plate form (experimental biological power generator).

[0107] In the biological power generator shown in FIG. 3, a plurality of three-layered tubular elements (power generating units) which, as shown in FIG. 2, are each composed of an anode 51 as an inner tube, a diaphragm 52, and a cathode 53 as an outer tube, are located within an air compartment 57 formed of an outer shell. The substrate is injected for distribution into the interiors 54 of the plurally arranged power generating units 54 via an inflow section 59 by means of an inflow pump. After undergoing oxidative decomposition therein, the substrate leaves the reaction vessel via an effluent section 60 and is discharged to the outside of the system as a treated liquid 6. The microbial cell bodies and sludge accumulating in the reaction vessel are discharged by opening an excess sludge discharge port 63 with times. In addition, by injecting water, an inert gas, and an anaerobic gas through the same discharge port 63, the inside of the reaction vessel can be back-washed and air-washed. Any anaerobic gas that evolves within the reaction vessel can be discharged through an exhaust vent 69. The evolved anaerobic gas may be stored for use in air washing.

[0108] Regarding the porous cathode 53, it may be supplied with oxygen by introducing air into the air compartment 57 via an air intake port 64 using a blower. However, if the use does not require forced ventilation, the air compartment 57 may be removed to construct an apparatus in which the cathode 53 forming the outer tube of each power generating unit contacts external air. The introduced air flows through the space 55 between adjacent power generating units in the air compartment 57 and contacts each cathode 53 before it is discharged through an exhaust vent 65. In addition, the water produced by the reduction reaction at the cathode 53 is either discharged through the exhaust vent 65 as water vapor or is discharged through a condensed water drain 66 as condensed water.

[0109] A conductor wire 56 is electrically connected to the inner tubes of the plural power generating units by means of connections 67 to the anodes, and to the outer tubes of the plural power generating units by means of connections 68 to the cathodes 53. In this case, it is necessary that the conductor wire 56 be electrically isolated from the surrounding environment to ensure that neither electrical shorting nor oxidation-reduction on the surface of the conductor wire take place.

[0110] The apparatus shown in FIG. 3 may also be adapted in the same way as explained above in connection with FIG. 2, i.e., each power generating unit is constructed as a tubular element such that the cathode forms the inner tube and the anode the outer tube, with air being supplied into the space within each tubular element and with the substrate being brought into contact with the anode outside the tubular element of each power generating unit.

[0111] One of the goals to be attained by the cathode is to enhance efficiency of the reduction reaction of oxygen on the electrode. To this end, at least a part of the cathode is preferably formed of an electrically conductive porous material, net-like or fibrous material that have voids in their structure such that the cathode is caused to contact with air, with a contact interface between the air and water occurring within voids in the cathode, whereby an efficiency of contact with the oxygen in the air and the water at the water surface is increased.

[0112] FIG. 4 shows in section an exemplary cathode structure that may be adopted in the biological power generator. FIG. 4(A) shows a section of the structures of the diaphragm 52 and the cathode 53 and FIG. 4(B) is a view of FIG. 4 (A) as viewed from the air compartment 55. Note that the reaction system shown in FIG. 4 is one where the diaphragm 52 is a cation-exchange membrane. The cathode shown in FIG. 4 is of such a structure that a porous matrix 20 has supported thereon a catalyst 21 comprising an alloy or compound that preferably contains at least species selected from among platinoids, silver and transition metal elements (FIG. 4(A)), and it assumes a network structure as seen from the air compartment 55 (FIG. 4(B)). By adopting this structure, the cathode 53 can be brought into contact with the oxygen in the air while the water that is either at the water surface or passing through the diaphragm is drawn up by the hydrophilicity of the substrate, so that an air network 22 and an aqueous solution network 23 are introduced into the

microscopic structure of the electrode to thereby increase the area of the air/water contact interface and enhance the efficiency of contact with the oxygen in the air and the water at the water surface. The oxygen reacting with hydrogen ions on the catalyst 21 enables promoting the reduction reaction of the oxygen in the air.

[0113] FIG. 4(C) shows in section another exemplary cathode structure that may be adopted in the biological power generator. Again, the reaction system shown in FIG. 4(C) is one where the diaphragm 52 is a cation-exchange membrane. To construct the cathode shown in FIG. 4(C), a solution made of the same materials as the diaphragm 52 is coated on the side of the porous matrix 20 which is joined to the diaphragm 52 and then dried, whereby part of the diaphragm's structure is allowed to get into fine pores in the porous matrix 20. By adopting this structure, the utilization of ion exchange and that of the catalyst can be improved to promote the reduction reaction of the oxygen in the air.

[0114] We next describe the method of treating organic solid pollutant-containing waste with the treatment apparatus shown in FIG. 1. In the treatment apparatus shown in FIG. 1, an organic solid pollutant-containing waste 1 is held in the raw water reservoir 2 and then a liquid feed pump is activated to transfer the organic solid pollutant-containing waste 1 into the solubilizing vessel 3. In the solubilizing vessel 3, either one of the means selected from among the mechanical solubilizing treatment by mechanical crushing with a mill or a stone mortar or by ultrasonic crushing, the physical solubilizing treatment by steaming or blasting, the solubilizing treatment by hydrothermal electrolysis, and the solubilizing treatment with a chemical substance such as an acid, alkali, ozone, hypochlorous acid or hydrogen peroxide is applied, whereby the organic solid pollutant-containing waste 1 is converted to a solubilized liquid under treatment that contains solubilized organic substances.

[0115] Subsequently, the solubilized liquid under treatment is fed into the anaerobic region 5a of the biological power generator 5 by means of a liquid feed pump. On the other hand, the aerobic region 5b of the biological power generator 5 is supplied with oxygen humidified to have a relative humidity of 100% or oxygen-containing air. In this case, a pump or a fan may be used to pass the oxygen or the oxygen-containing air into the aerobic region 5b of the biological power generator 5 or, alternatively, heat convection may be utilized for the same purpose.

[0116] On the basis of the pH, measured with the pH controller 8, of the solubilized liquid under treatment in the anaerobic region 5a of the biological power generator 5, a pH adjusting chemical (acid, alkali, or pH buffer) is supplied from the pH adjusting chemical solution reservoir 7 into the anaerobic region 5a of the biological power generator 5, whereupon the pH of the liquid in the anaerobic region 5a of the biological power generator 5 is maintained within a range of 10.5 to 6.5. The temperature of the solubilized liquid under treatment in the anaerobic region 5a is maintained at a level that maintains the activity of electrode-active microorganisms, for instance, at 10°C to 45°C. Under this condition, the solubilized liquid under treatment is passed through the anaerobic region 5a with a residence time of 24 to 240.

[0117] Thereafter, the treated liquid 6 is discharged from the anaerobic region 5a of the biological power generator 5 via a discharge port. Depending on need, the treated liquid 6 may be subjected to a variety of post-treatments (for example, a treatment such as flocculation and precipitation, filtering through activated carbon, treatment with aerobic microorganisms, phosphate removal, denitrification, or sulfate reduction).

[0118] FIG. 5 is a flow chart depicting another mode of embodiment for the treatment apparatus of the present invention. Those parts of the construction which overlap with the treatment apparatus of FIG. 1 will not be explained.

[0119] The treatment apparatus shown in FIG. 5 further includes a polymer-degradation vessel 103 between the solubilizing vessel 3 and the biological power generator 5. The polymer-degradation vessel 103 has a pH control mechanism that comprises a pH controller 8a and piping through which an alkaline solution is recovered from the aerobic region 5b of the biological power generator 5 and circulated to the low-molecular-weight realizing vessel 103. Advantageously, water feed piping (not shown) is connected to the aerobic region 5b and piping is also provided such that an alkaline solution as generated within the aerobic region 5b is recovered by overflow into an alkaline solution reservoir 10, and the same alkaline solution is circulated from the alkaline solution reservoir 10 to the polymer-degradation vessel 103 by means of the pH controller 8a which performs control on the basis of a signal from the pH measurement of the solubilized liquid under treatment in the polymer-degradation vessel 103; the pH adjusting chemical reservoir 7 is so constructed that the alkaline solution is fed only to the anaerobic region 5a of the biological power generator 5.

[0120] FIG. 6 is a flow chart depicting yet another embodiment of the treatment apparatus of the present invention. Those parts of the construction which overlap the treatment apparatus of FIG. 1 will not be explained.

[0121] The treatment apparatus shown in FIG. 6 includes an aeration vessel 12 that receives the treated water 6 from the biological power generator 5 and subjects it to an aeration treatment, a precipitation vessel 13 which receives the treated water after it has been aerated in the aeration vessel 12 and which then performs solid-liquid separation into secondary treated water 14 and sludge 15, piping 16 through which part of the excess sludge 15 that has precipitated in the precipitation vessel 13 is circulated to the aeration vessel 12, and piping 17 for circulating part of the excess sludge 15 to the solubilizing vessel 3. The secondary treated water 14 and the excess sludge 15 that result from the treatment in the precipitation vessel 13 are discharged.

<Polymer-degradation treatment>

[0122] FIG. 8 is a flow chart of an apparatus for treating an organic polymeric substance-containing liquid waste according to the second aspect of the present invention which relates to the treatment of organic waste. In FIG. 8, the treatment apparatus of the present invention includes a polymer-degradation vessel 103 and a biological power generator 5 comprising an anaerobic region 5a and an aerobic region 5b that are defined by a diaphragm 5c. Connected between the polymer-degradation vessel 103 and the biological power generator 5 are piping 104 and a pump for feeding a liquid of a smaller molecular weight under treatment to the biological power generator 5. Connected to the polymer-degradation vessel 103 are piping from a pH adjusting chemical reservoir 7 and piping from a pH controller 8a, and connected to the anaerobic region 5a of the biological power generator 5 are piping from the pH adjusting chemical reservoir 7 and piping from a pH controller 8b. A raw water reservoir 2 for holding an organic polymeric substance-containing liquid waste 101 is connected to the polymer-degradation vessel 103 via piping and a pump. The other parts of the system are constructed in the same way as described in connection with the first aspect of the present invention.

[0123] Next is described the method of treating the organic polymeric substance-containing liquid waste with the treatment apparatus shown in FIG. 8. In the treatment apparatus shown in FIG. 8, the organic polymeric substance-containing liquid waste 101 is held in the raw water reservoir 2 and then a liquid feed pump is activated to transfer the organic polymeric substance-containing liquid waste 101 into the polymer-degradation vessel 103. In the polymer-degradation vessel 103, organic polymeric substance decomposing anaerobic microorganisms are present and on the basis of the pH, measured with the pH controller 8, of the liquid under treatment in the polymer-degradation vessel 103, a pH adjusting chemical (acid, alkali, or pH buffer) is supplied from the pH adjusting chemical solution reservoir 7 into the polymer-degradation vessel 103, whereupon the pH of the liquid under treatment in the polymer-degradation vessel 103 is maintained within a range of 4.0 to 6.5. The temperature of the liquid under treatment in the polymer-degradation vessel 103 is maintained at a level that maintains the activity of the organic polymeric substance decomposing anaerobic microorganisms, for instance, at a moderate temperature of 30°C to 40°C or at a high temperature of 50°C to 60°C. Under this condition, the organic polymeric substance-containing liquid waste 101 is allowed to stay within the polymer-degradation vessel 103 for 4 hours to 96 hours, whereby the organic polymeric substance decomposing anaerobic microorganisms decompose the organic polymers to monosaccharides, oligo-saccharides, amino acids and peptides, which are further decomposed to volatile organic acids, whereupon a liquid of smaller molecular weight under treatment is formed.

[0124] Subsequently, the liquid of smaller molecular weight under treatment is fed into the anaerobic region 5a of the biological power generator 5 by means of a liquid feed pump. On the other hand, the aerobic region 5b of the biological power generator 5 is supplied with oxygen humidified to have a relative humidity of 100% or oxygen-containing air. In this case, a pump or a fan may be used to pass the oxygen or the oxygen-containing air into the aerobic region 5b of the biological power generator 5 or, alternatively, heat convection may be utilized for the same purpose.

[0125] On the basis of the pH, measured with the pH controller 8b, of the liquid of smaller molecular weight under treatment in the anaerobic region 5a of the biological power generator 5, a pH adjusting chemical (acid, alkali, or pH buffer) is supplied from the pH adjusting chemical solution reservoir 7 into the anaerobic region 5a of the biological power generator 5, whereupon the pH of the liquid in the anaerobic region 5a of the biological power generator 5 is maintained within a range of 10.5 to 6.5. The temperature of the liquid of smaller molecular weight under treatment in the anaerobic region 5a is maintained at a level that maintains the activity of the electrode-active microorganisms, for instance, at 10°C to 45°C. Under this condition, the liquid of smaller molecular weight under treatment is passed through the anaerobic region 5a with a residence time of 24 hours to 240 hours.

[0126] Thereafter, the treated liquid 6 is discharged from the anaerobic region 5a of the biological power generator 5 via a discharge port. Depending on need, the treated liquid 6 may be subjected to a variety of post-treatments (for example, a treatment such as flocculation and precipitation, filtering through activated carbon, treatment with aerobic microorganisms, phosphate removal, denitrification, or sulfate reduction).

[0127] FIG. 9 is a flow chart depicting another mode of embodiment for the treatment apparatus of the present invention. Those parts of the construction which overlap the treatment apparatus of FIG. 8 will not be explained.

[0128] The treatment apparatus shown in FIG. 9 further includes a mechanism for recovering an alkaline solution from the aerobic region 5b of the biological power generator 5 and circulating it to the polymer-degradation vessel 103. Specifically, water feed piping (not shown) is connected to the aerobic region 5b and piping is also provided such that an alkaline solution as generated within the aerobic region 5b is recovered by overflow into an alkaline solution reservoir 10 and the same alkaline solution is circulated from the alkaline solution reservoir 10 to the polymer-degradation vessel 103 by means of the pH controller 8 which performs control on the basis of a signal from the pH measurement of the liquid waste 101 in the polymer-degradation vessel 103; the pH adjusting chemical reservoir 7 is so constructed that the alkaline solution is fed only to the anaerobic region 5a of the biological power generator 5.

[0129] If the treatment method and apparatus of the present invention are to be used to treat organic solid waste, the solid waste may be reduced to fine particles preliminarily by means of a separate treatment vessel that is provided

upstream of the polymer-degradation vessel 103. If desired, a post-treatment device may be provided to perform a further enhanced treatment of the treated liquid 6 that has been discharged from the biological power generator 5. Examples of the post-treatment device that can be used include an activated sludge treatment vessel for further reducing the concentration of organic matter in the treated liquid, a biological treatment vessel for removing nutrient salts such as nitrogen and phosphorus from the treated liquid, or a chemical treatment vessel.

<Post-treatment>

[0130] FIG. 10 is a flow chart depicting an apparatus for treating organic pollutant-containing liquid waste according to the third aspect of the present invention which relates to the treatment of organic waste. In FIG. 10, the treatment apparatus of the present invention includes a biological power generator 5 and a post-treatment vessel 310, the biological power generator 5 comprising an anaerobic region 5a and an aerobic region 5b that are defined by a diaphragm 5c. The post-treatment vessel 310, the choice of which depends on the properties of an organic pollutant-containing liquid waste 1, may be a flocculation and precipitation vessel, an activated carbon assisted filtering vessel, an aerobic microbial decomposition vessel, an anaerobic microbial decomposition vessel, a denitrification vessel, a dephosphorylation vessel, or a sulfate reduction vessel. Connected between the biological power generator 5 and the post-treatment vessel 310 are piping 6 and a pump for feeding the treated liquid to the post-treatment vessel 310. Connected to the anaerobic region 5a of the biological power generator 5 are piping from a pH adjusting chemical reservoir 7 and piping from a pH controller 8. The treatment apparatus shown in FIG. 10 is equipped with a raw water reservoir 2 for holding the organic pollutant-containing liquid waste 301, as well as piping and a pump for feeding the organic pollutant-containing liquid waste 301 from the raw water reservoir 2 into the biological power generator 5. The other parts of the system are constructed in the same way as described in connection with the first aspect of the present invention.

[0131] Next is described the method of treating the organic pollutant-containing liquid waste with the treatment apparatus shown in FIG. 10. In the treatment apparatus shown in FIG. 10, the organic pollutant-containing liquid waste 301 is held in the raw water reservoir 2 and then a liquid feed pump is activated to feed the organic pollutant-containing liquid waste 301 into the anaerobic region 5a of the biological power generator 5. On the other hand, the aerobic region 5b of the biological power generator 5 is supplied with oxygen humidified to have a relative humidity of 100% or oxygen-containing air. In this case, a pump or a fan may be used to pass the oxygen or the oxygen-containing air into the aerobic region 5b of the biological power generator 5 or, alternatively, heat convection may be utilized for the same purpose.

[0132] On the basis of the pH, measured with the pH controller 8, of the organic pollutant-containing liquid waste in the anaerobic region 5a of the biological power generator 5, a pH adjusting chemical (acid, alkali, or pH buffer) is supplied from the pH adjusting chemical solution reservoir 7 into the anaerobic region 5a of the biological power generator 5, whereupon the pH of the liquid in the anaerobic region 5a of the biological power generator 5 is maintained within a range of 10.5 to 6.5. The temperature of the organic pollutant-containing liquid waste in the anaerobic region 5a is maintained at a level that maintains the activity of the electrode-active microorganisms, for instance, at 10°C to 45°C. Under this condition, the organic pollutant-containing liquid waste is passed through the anaerobic region 5a with a residence time of 24 hours to 240 hours.

[0133] Thereafter, the treated liquid 6 is discharged from the anaerobic region 5a of the biological power generator 5 via a discharge port into the post-treatment vessel 310, where it is subjected to a post-treatment such as flocculation and precipitation, filtering through activated carbon, aerobic microbial decomposition, anaerobic microbial decomposition, phosphate removal, denitrification or sulfate reduction, whereupon the pollution load index of secondary treated water 311 is reduced to a level below the emission standard.

[0134] FIG. 11 is a flow chart depicting another mode of embodiment for the treatment apparatus according to the third aspect of the present invention which relates to the treatment of organic waste. Those parts of the construction which overlap the treatment apparatus of FIG. 10 will not be explained.

[0135] The treatment apparatus shown in FIG. 11 further includes a polymer-degradation vessel 103 provided between the raw water reservoir 2 and the biological power generator 5. The polymer-degradation vessel 103 has a pH controller 8a and is connected to piping for feeding an alkaline solution from a pH adjusting chemical reservoir 7. The pH adjusting chemical reservoir 7 feeds an alkali chemical to both the anaerobic region 5a of the biological power generator 5 and the polymer-degradation vessel 103.

[0136] Next is described the treatment of an organic pollutant-containing liquid waste 1 in the treatment apparatus shown in FIG. 11. The organic pollutant-containing liquid waste 1 is transferred from the raw water reservoir 2 into the polymer-degradation vessel 103. In the polymer-degradation vessel 103, anaerobic microorganisms capable of decomposing organic pollutants (organic pollutant decomposing anaerobic microorganisms) are present and on the basis of the pH, measured with the pH controller 8a, of the organic pollutant-containing liquid waste 1 in the polymer-degradation vessel 103, a pH adjusting chemical (acid, alkali, or pH buffer) is supplied from the pH adjusting chemical solution reservoir 7 into the polymer-degradation vessel 103, whereupon the pH of the organic pollutant-containing liquid waste 1 in the polymer-degradation vessel 103 is maintained within a range of 4.0 to 6.5. The temperature of the organic

pollutant-containing liquid waste 1 in the polymer-degradation vessel 103 is maintained at a level that maintains the activity of the organic pollutant decomposing anaerobic microorganisms, for instance, at 10°C to 45°C. Under this condition, the organic pollutant-containing liquid waste 1 is allowed to stay within the polymer-degradation vessel 103 for 24 hours to 240 hours, whereby the organic pollutant decomposing anaerobic microorganisms decompose the organic pollutants to monosaccharides, oligo-saccharides, amino acids and peptides, which are further decomposed to volatile organic acids, whereupon a liquid under treatment of a smaller molecular weight is formed.

[0137] Subsequently, the liquid of smaller molecular weight under treatment is fed into the anaerobic region 5a of the biological power generator 5 by means of a liquid feed pump. On the other hand, the aerobic region 5b of the biological power generator 5 is supplied with oxygen humidified to have a relative humidity of 100% or oxygen-containing air. In this case, a pump or a fan may be used to pass the oxygen or the oxygen-containing air into the aerobic region 5b of the biological power generator 5 or, alternatively, heat convection may be utilized for the same purpose.

[0138] On the basis of the pH, measured with the pH controller 8, of the liquid of smaller molecular weight under treatment in the anaerobic region 5a of the biological power generator 5, a pH adjusting chemical (acid, alkali, or pH buffer) is supplied from the pH adjusting chemical solution reservoir 7 into the anaerobic region 5a of the biological power generator 5, whereupon the pH of the liquid in the anaerobic region 5a of the biological power generator 5 is maintained within a range of 10.5 to 6.5. The temperature of the liquid of smaller molecular weight under treatment in the anaerobic region 5a is maintained at a level that maintains the activity of the electrode-active microorganisms, for instance, at 10°C to 45°C. Under this condition, the liquid of smaller molecular weight under treatment is passed through the anaerobic region 5a with a residence time of 24 hours to 240 hours.

[0139] Thereafter, the treated liquid 6 is discharged from the anaerobic region 5a of the biological power generator 5 via a discharge port into the post-treatment vessel 310, where it is subjected to a post-treatment as described with reference to FIG. 10, whereupon secondary treated water 311 is obtained.

[0140] FIG. 12 is a flow chart depicting yet another mode of embodiment for the treatment apparatus according to the third aspect of the present invention which relates to the treatment of organic waste. Those parts of the construction which overlap the treatment apparatuses of FIG. 10 and FIG. 11 will not be explained.

[0141] The treatment apparatus shown in FIG. 12 further includes a post-treatment vessel 410 that receives the treated water 6 from the anaerobic region 5a of the biological power generator 5 for post-treatment. The post-treatment vessel 410 is the second biological power generator. The post-treatment vessel 410 is partitioned into an anaerobic region 410a and an aerobic region 410b by a diaphragm 410c. The anaerobic region 410a is provided with an anode (not shown) having an electron mediator immobilized thereon and having a higher standard electrode potential than the anode (not shown) provided in the anaerobic region 5a of the biological power generator 5. The anaerobic microorganisms contained in the anaerobic region 410a may be the same as those used in the biological power generator 5. The diaphragm 410c may also be the same as that used in the biological power generator 5. The aerobic region 410b may also be constructed in the same way as the aerobic region 5b of the biological power generator 5, except that the anode and the cathode are directly wire-connected so that almost all electric power that is generated by transfer of electrons between the anode and cathode is consumed by the oxidation of the electron mediator at the anode. The anaerobic region 410a has connected thereto piping from the pH adjusting chemical reservoir 7 and piping from the pH controller 8b.

[0142] The method of treating an organic pollutant-containing liquid waste 1 in the treatment apparatus shown FIG. 12 is performed in the same mode as explained in connection with FIG. 11. The treated water 6 from the anaerobic region 5a of the biological power generator 5 is transferred to the anaerobic region 410a of the post-treatment vessel 410. The pH of the treated water 6 in the anaerobic region 410a of the post-treatment vessel 410 is controlled by the pH controller 8b to be within a range of 6.5 to 10.5. The temperature of the treated water 6 in the anaerobic region 410a is maintained at a level that maintains the activity of the electrode-active microorganisms, for instance, at 10°C to 45°C. Under this condition, the treated water 6 is passed through the anaerobic region 410a with a residence time of 24 hours to 240 hours, whereupon a pollution load index, in particular BOD, of secondary treated water 411 is reduced to a level below the emission standard.

[0143] In the illustrated mode of embodiment, the secondary treated water 411 is discharged as it is but if the polluting index of the secondary treated water 411 does not meet the environmental standard, the system may be so modified as to perform a further post-treatment by including piping and a pump for effecting circulation to the post-treatment vessel 410; alternatively, different types of post-treatment vessel 410 may be connected together by means of piping and pumps.

[0144] The modes of embodiment shown in FIG. 11 and FIG. 12 employ the polymer-degradation vessel 103 but if desired, the solubilizing vessel 3 may be used in place of, or in addition to, the polymer-degradation vessel 103. In the solubilizing vessel 3, either one of the means selected from among the mechanical solubilizing treatment by mechanical crushing with a mill or a stone mortar or by ultrasonic crushing, the physical solubilizing treatment by steaming or blasting, the solubilizing treatment by hydrothermal electrolysis, and the solubilizing treatment with a chemical substance such as an acid, alkali, ozone, hypochlorous acid or hydrogen peroxide is applied, whereby the organic solid pollutant-containing liquid waste 1 is converted to an organic pollutant-containing liquid waste that contains solubilized organic substances. This mode is advantageous for a case where the organic pollutants are solids that are difficult to dissolve,

disperse or suspend in media.

EXAMPLES

[0145] In the following pages, the present invention is described specifically by means of examples. It should, however, be understood that the present invention is in no way limited by these examples.

[Example 1] (Heat Treatment)

[0146] Using the experimental biological power generator 5 shown in FIG. 7, the treatment apparatus of the present invention shown in FIG. 1 (with the solubilizing vessel 3 being installed upstream of the biological power generator 5) was operated to treat an organic solid pollutant-containing waste (Example 1) and the performance of this system in water treatment and power generation was compared with a case where the organic solid pollutant-containing waste was treated using only the experimental biological power generator 5 shown in FIG. 7 (Control).

<Biological power generator>

[0147] As shown in FIG. 7, the biological power generator 5 was a stacked structure (power generating unit) in which a cell frame 37 measuring 200 mm (inside dimension, 180 mm) long on each side and 50 mm (inside dimension, 40 mm) in thickness and serving to form an anode compartment as an anaerobic region was placed adjacent a cell frame 38 measuring 200 mm long on each side and 20 mm in thickness, and serving to form a cathode compartment as an aerobic region. Engraved within the cell frame 38 were columnar gas channels commonly used as the air electrode in fuel cells. Inside the stack of the cell frames 37 and 38, an anode 51, a diaphragm 52 and a cathode 53 were successively bonded by the hot press method (with pressure applied at an elevated temperature of 100°C to 200°C) which is commonly applied for fuel cells, to thereby form an anaerobic region 5a within the cell frame 37 and an aerobic region 5b within the cell frame 38. Although not shown, the anode 51 and cathode 53 were electrically connected by a conductor wire to form a closed circuit with an ammeter (power utilizing device) inserted.

[0148] The external circuit including the ammeter in the biological power generator shown in FIG. 7 had a resistance of about 1 Ω, with the internal resistance being approximately 50 Ω. The anaerobic region 5a had 20 mL of an electrode-active microorganism enriched culture added to it before starting the operation.

[0149] The anode, diaphragm and the cathode used in Example 1 are described below.

<Anode>

[0150] Carbon paper (EC-TP1-060 of Electrochem, Inc.) was used as an anode material, and anthraquinone-2,6-disulfonic acid (AQ-2,6-DS) was used as an electron mediator to be immobilized on the anode.

[0151] Commercial AQ-2,6-DS was subjected to reaction for an hour under the 70°C condition in an acetonitrile containing sulfolane and phosphorus oxychloride in amounts corresponding to half a mole with respect to AQ-2,6-DS, whereby the sulfonic acid groups were converted to an acid chloride. The reaction product was filtered under cooling with ice, washed with iced water, and then dried to afford a powder of AQ-2,6-DS chloride.

[0152] In a separate step, commercial Vulcan XC-72R (Cabot) carbon black was sampled in 10 g and 10 mmol each of sulfanilic acid and a nitrite was allowed to act on the carbon black, whereupon sulfonic acid groups were introduced into it by the diazo coupling reaction. Using oxalyl chloride, the introduced sulfonic acid groups were converted to sulfonyl chloride. Further, in the solvent THF (tetrahydrofuran), 1,3-propanediamine was acted on the carbon black to introduce amino groups into its surface. The density of the amino groups introduced in the resulting aminated carbon black was determined by titration, giving a value of 500 μmol/g.

[0153] Twenty grams of the resulting aminated carbon black, 100 mmol of the AQ-2,6-DS chloride, and 8 mL of triethylamine were subjected to reaction in the solvent DMF (dimethylformamide) at 50°C for 24 hours, and the reaction product was dried. The dried reaction product was dispersed in an isopropanol solution of 5% Nafion (registered trademark), coated on carbon paper (EC-TP1-060 of Electrochem, Inc.), and dried.

[0154] Using the above-mentioned anode with AQ-2,6-DS immobilized on it, an electric potential was applied in an aqueous solution at pH 7 as it was shifted from -0.20 V up to -0.15 V (hydrogen's standard electrode potential) at a rate of 20 mV/sec, whereupon an electric current was produced; hence, it may be concluded that the anode of interest has a standard electrode potential E_0' between -0.20 V and -0.15 V.

<Diaphragm>

[0155] A cation-exchange membrane (Nafion 115 manufactured by DuPont: registered trademark of DuPont) was

used as the diaphragm 52.

<Cathode>

[0156] The cathode 53 was a combination of catalyst-supporting carbon paper 53a and a collector 53b, with the carbon paper 53a being prepared by coating a slurry of platinum-supporting carbon black and an isopropanol solution of 5% Nafion (registered trademark of DuPont) onto carbon paper (EC-TP1-060 of Electrochem, Inc.) and drying the coat.

<Organic solid pollutant-containing waste>

[0157] In Example 1, excess sludge collected from a sewage treatment plant was used as an organic solid pollutant-containing waste.

<Electrode-active microorganism enriched culture>

[0158] KUROBOKU (Andosol) soil (0.1 g) was used as an inoculum source; the Desulfuromonas medium (Table 5) described in Handbook of Microbial Media (Atlas et al., 1997, CRC Press) was injected in 100 mL into a vial with a capacity of 130 mL and the gas phase was replaced by nitrogen gas; the inoculum was added to the thus treated medium; the vial was then sealed and shake culture was performed under the temperature condition of 28°C; after two weeks, 5 mL of the bacterial liquor obtained was subcultured in a freshly treated vial; this procedure was repeated five times and the bacterial liquor obtained in 10 weeks was used as an electrode-active microorganism enriched culture. Note that the soil as the inoculum source is not particularly limited to Kuroboku soil and may be replaced by loam or silt.

[0159] [Table 5]

Table 5 Composition of Desulfuromonas Medium (pH 7.2±0.2)

Sulfur (colloidal)		10 g
Nutrient Liquid 1	(KH_2PO_4 1g, $MgCl_2 \cdot 6H_20$ 0.4 g, NH_4Cl 0.3 g, $CaCl_2 \cdot H_2O$ 0.1 g, 2 mol/L-HCl 4.0 mL) in 1 L	1 L
Nutrient Liquid 3	($NaHCO_3$ 10 g) in 100 mL	20 mL
Nutrient Liquid 4	($Na_2S \cdot 9H_2O$ 5 g) in 100 mL	6 mL
Nutrient Liquid 5	(pridoxamine dihydrochlorate 0.01 g, nicotinic acid 4 mg, p-aminobenzoic acid 2 mg, thiamine 2 mg, cyanocobalamin 1 mg, calcium pantothenate 1 mg, biotin 0.5 mg) in 200 mL	5 mL
Nutrient Liquid 2	(EDTA disodium salt 5.2 g, $CoCl_2 \cdot 6H_2O$ 1.9 g, $Fe_2Cl \cdot 4H_2O$ 1.5 g, $MnCl_2 \cdot 4H_2O$ 1 g, $ZnCl_2$ 0.7 g, H_3BO_3 0.62 g, $Na_4MoO_4 \cdot 2H_2O$ 0.36 g, $NiCl_2 \cdot 6H_2O$ 0.24 g, $CuCl_2 \cdot 2H_2O$ 0.17 g) in 1 L	1 mL

<Treatment test>

[0160] In Experimental system 1, the sludge as the organic solid pollutant-containing waste was solubilized by 150°C x 30 min heat treatment in the solubilizing vessel 3 before it was fed into the anaerobic region 5a of the biological power generator 5 shown in FIG. 7. In a control system, excess sludge was directly fed into the anaerobic region 5a of the biological power generator 5 shown in FIG. 7.

[0161] In the biological power generator 5, no replacemant of the liquid in the anaerobic region (microbial reaction compartment) was carried out for 10 days after the start of operation so that the microorganisms would adhere to the inside walls of the anaerobic region in the process but, instead, the Desulfuromonas medium (Table 5) described in Handbook of Microbial Media (Atlas et al., 1997, CRC Press) was loaded into the anaerobic region 5a (microbial reaction compartment) so that sulfur-reducing bacteria (electrode-active microorganisms) would become predominant (the conditioning period) to provide a condition in preparation for the subsequent system operation.

[0162] For a period of 10 days after the start of continuous injection of solubilized liquid under treatment from the solubilizing vessel 3 into the anaerobic region 5a of the biological power generator 5, the biological power generator was operated with the solubilized liquid under treatment staying in the biological power generator 5 for a residence time of 30 days (the fixing period). Starting 60 days after it started to run, the biological power generator was shifted to normal operation with the liquid of smaller molecular weight under treatment staying in the anaerobic region 5a for a residence

time of 15 days, during which period the amount of current flowing between anode and cathode and the voltage across the two electrodes were measured.

[0163] In Example 1, the cathode and the anode were kept electrically connected at all times including the conditioning and fixing periods.

[0164] The influents into the biological power generators in Experimental system 1 and Control system 1 were measured for the solids (TSS) concentration, volatile solids (VSS) concentration, total CODcr (T-CODcr) concentration, and centrifuged (10000 rpm, 15 min) supernatant CODcr (S-CODcr) concentration (in accordance with the Industrial Effluent Test Method under JIS K0102), and they were also subjected to HPLC (SHIMADZU) for measurement of the organic acids concentration in the filtrate; the results of the measurements are shown in Table 6.

[0165] [Table 6]

Table 6 Properties of Influents into Biological Power Generators in the Experimental System and the Control System

	Experimental System 1	Control System 1
SS (mg/L)	12,200	13,800
VSS (mg/L)	9,770	11,900
T-CODcr (mg/L)	23,300	23,300
S-CODcr (mg/L)	4,400	580
Organic acids (mg/L)	3,960	188

[0166] The biological power generator was supplied with the solubilized liquid under treatment (Experimental system 1) or sludge as the organic solid sludge substance-containing waste (Control system 1), which were passed through the anaerobic region 5a that had been adjusted to a pH of approximately 7; the treated liquid 6 was then discharged through the treated liquid discharge port. Humidified air adjusted to have a relative humidity of 100% was fed into the aerobic region 5b via the air intake port 64; the humidified air passing through the aerobic region 5b was discharged through the exhaust vent 66. An excess alkaline aqueous solution generated in the aerobic region 5b was washed down by flowing a small amount of water with times and then recovered.

[0167] The effective capacity of the apparatus under consideration was 1500 mL for the anaerobic region 5a (microbial reaction compartment) and 500 mL for the aerobic region 5b (air reaction compartment); the feed rate was so adjusted that the liquid under treatment would have a residence time of 15 days and the air a residence time of 1 minute. The total electrode surface area was set at 300 cm^2 for both anode and cathode. The experiments were conducted in a constant-temperature bath with 30°C.

[0168] In both Experimental system 1 and Control system 1, the current density and voltage gradually changed during a period of about 30 days (approximately twice the residence time) after the start of operation but in Experimental system 1, the current density stabilized at approximately 3.5 A/m^2 and the voltage at approximately 0.5 V. In Control system 1, on the other hand, the current density stabilized at about 1.2 A/m^2 and the voltage at approximately 0.3 V. The results are shown in Table 7.

[0169] [Table 7]

Table 7 Treatment Performance During Stable Operation (Average for 60 Days)

	Experimental System 1	Control System 1
Current density (A/m^2)	3.5	1.2
Voltage (V)	0.5	0.3
T-CODcr removal (%)	35.9	12.3

[Example 2] [Mechanical Treatment]

[0170] Using, as in Example 1, the experimental biological power generator 5 shown in FIG. 7, the treatment apparatus shown in FIG. 2 (with the solubilizing vessel 3 and the polymer-degradation vessel 103 being installed upstream of the biological power generator 5) was operated to effect treatment (Experimental system 2) and the performance of this system in water treatment and power generation was compared with the case where treatment was effected with the treatment apparatus shown in FIG. 2, except that it did not include the solubilizing vessel 3 (Control system 2).

<Organic solid pollutant-containing waste>

[0171] Coffee grounds were used as an organic solid pollutant-containing waste.

[0172] In Experimental system 2, the coffee grounds in the solubilizing vessel 3 were crushed on a stone mortar into particles having an average size of 300 μm. Then, 10 g of the crushed product was suspended in 1 L of tap water, charged into a jar fermenter (polymer-degradation vessel 103), inoculated with sludge collected from the acid fermentation tank in a garbage treating two-phase methane fermenter, and reduced in molecular weight by treatment at pH of 5.0-6.0 and 35°C for 48 hours at an agitation speed of 50 rpm. In Control system 2, 10 g of coffee grounds were used after being reduced in molecular weight by the same treatment as in Experimental system 2, except that they were not crushed into smaller particles but suspended in 1 L of tap water as it is.

[0173] The influents into the biological power generators in Experimental system 2 and Control system 2 were measured for the solids (SS) concentration, volatile solids (VSS) concentration, total CODcr (T-CODcr) concentration, and centrifuged (10000 rpm, 15 min) supernatant CODcr (S-CODcr) concentration, and they were also subjected to HPLC (SHIMADZU) for measurement of the organic acids concentration in the filtrate; the results of the measurements are shown in Table 8.

[0174] [Table 8]

Table 8 Properties of Influents into Biological Power Generators in the Experimental System and the Control System

	Experimental System 2	Control System 2
SS (mg/L)	11,190	11,835
VSS (mg/L)	11,160	11,580
T-CODcr (mg/L)	18,135	18,135
S-CODcr (mg/L)	6,480	4,275
Organic acids (mg/L)	3,890	1,035

[0175] As can be seen from Table 8, Experimental system 2 in which the solubilizing treatment was performed is such that the amount of CODcr in the supernatant and that of organic acids in the filtrate increased in comparison with Control system 2. This may lead to the conclusion that the solubilizing treatment contributed to making the organic solid pollutants more readily dispersible or dissolvable in a liquid.

[0176] The biological power generator was supplied with the solubilized liquid under treatment (Experimental system 2) or the organic solid sludge substance-containing waste that had not been subjected to the solubilizing treatment (Control system 2); the respective feeds were passed through the anaerobic region 5a that had been adjusted to a pH of approximately 7; the treated liquid 6 was discharged through the treated liquid discharge port. Humidified air adjusted to have a relative humidity of 100% was fed into the aerobic region 5b via the air intake port 64; the humidified air passing through the aerobic region 5b was discharged through the exhaust vent 66. An excess alkaline aqueous solution generated in the aerobic region 5b was washed down by flowing a small amount of water with times and then recovered.

[0177] The effective capacity of the apparatus under consideration was 1500 mL for the anaerobic region 5a (microbial reaction compartment) and 500 mL for the aerobic region 5b (air reaction compartment); the feed rate was so adjusted that the liquid under treatment would have a residence time of 40 days and the air a residence time of 1 minute. The total electrode surface was set at 300 cm^2 for both anode and cathode. The experiments were conducted in a constant-temperature bath with 30°C.

[0178] In both Experimental system 2 and Control system 2, the current density and voltage gradually changed during a period of about 20 days (approximately twice the residence time) after the start of operation but in Experimental system 2, about 20 days after the start of operation and onward, the current density stabilized at approximately 2.2 A/m^2 and the voltage at approximately 0.5 V. In Control system 2, on the other hand, the current density stabilized at about 1.2 A/m^2 and the voltage at approximately 0.2 V. The results are shown in Table 9.

[0179] [Table 9]

Table 9 Treatment Performance During Stable Operation

	Experimental System 2	Control System 2
Current density (A/m^2)	2.2	1.2
Voltage (V)	0.5	0.2
T-CODcr removal (%)	77.2	42.1

[Example 3]

[0180] Using, as the biological power generator 5, the experimental biological power generator shown in FIG. 7, the treatment apparatus of the present invention shown in FIG. 8 (with the polymer-degradation vessel being installed

upstream of the biological power generator) was operated to treat an organic polymeric substance-containing liquid waste (Experimental system 3) and the performance of this system in water treatment and power generation was compared with the treatment of the organic polymeric substance-containing liquid waste using only the experimental biological power generator shown in FIG. 7 (Control system 3).

<Organic polymer decomposing anaerobic microorganism enriched culture>

[0181] To prepare the organic polymer decomposing anaerobic microorganism enriched culture, 50 mL of a medium using glucose as a carbon source and having the composition shown in Table 10 below was injected into a nitrogen-purged 125-mL vial and after adding 1 mL of sludge from two-phase methane fermentation, enrichment culture was performed in a constant-temperature bath with 30°C for 2 days until an acid fermenting bacteria enriched culture was obtained.

[0182] [Table 10]

Table 10 Medium Using Glucose as Carbon Source

Ingredients	(mg)
Glucose	4000
Peptone	250
Yeast extract	500
Ammonium chloride	250
Sodium hydrogencarbonate	2500
Calcium chloride dihydrate	100
Dipotassium hydrogenphosphate	4000
Magnesium chloride hexahydrate	400
Tap water	1 L

<Treatment test>

[0183] The above-identified liquid waste from a food plant was put into a jar fermenter (polymer-degradation vessel 103) and inoculated with the enriched culture of organic polymer decomposing anaerobic microorganisms.

[0184] In the polymer-degradation vessel 103, the wastewater from a food plant that had been inoculated with the enriched culture of organic polymer decomposing microorganisms was maintained at pH of 5.0-6.0 while it was subjected to reaction at 35°C for 48 hours at an agitation speed of 50 rpm until the organic polymeric substances in the wastewater from a food plant were reduced in molecular weight. The thus obtained liquid of smaller molecular weight under treatment which contained the organic substances of smaller molecular weight was fed into the biological power generator 5 shown in FIG. 7

[0185] In the Control system, the liquid waste from a food plant was not passed through the polymer-degradation vessel 103 but was immediately fed into the biological power generator 5 shown in FIG. 7

[0186] In the biological power generator 5, no replacemant of the liquid in the anaerobic region (microbial reaction compartment) was carried out for 10 days after the start of operation so that the microorganisms would adhere to the inside walls of the anaerobic region in the process and, instead, the Desulfuromonas medium (Table 5) described in Handbook of Microbial Media (Atlas et al., 1997, CRC Press) was loaded into the anaerobic region 5a (microbial reaction compartment) so that sulfur-reducing bacteria (electrode-active microorganisms) would become predominant (the conditioning period) to provide a condition in preparation for the subsequent system operation.

[0187] For a period of 10 days after the start of continuous injection of liquid of smaller molecular weight under treatment from the polymer-degradation vessel 103 into the anaerobic region 5a of the biological power generator 5, the biological power generator was operated with the liquid of smaller molecular weight under treatment staying in the biological power generator 5 for a residence time of 10 days (the fixing period). Starting 20 days after it was started to run, the biological power generator was shifted to normal operation with the liquid of smaller molecular weight under treatment staying in the anaerobic region 5a for a residence time of 5 days, during which period the amount of current flowing between anode and cathode and the voltage across the two electrodes were measured.

[0188] In Example 3, the cathode and the anode were kept electrically connected at all times, including the conditioning and fixing periods.

[0189] The influents into the biological power generators in Experimental system 3 and Control system 3 (the influent was the liquid of smaller molecular weight under treatment in Experimental system 3) were measured for the CODcr concentration (in accordance with the Industrial Effluent Test Method under JIS K0102), and the concentrations of organic

acids in the filtrate were also measured by HPLC (SHIMADZU); the results are shown in Table 11.

[0190] [Table 11]

Table 11 Principal Organic Acids and CODcr Concentration in Influents into Biological Power Generators in the Experimental System and the Control System

	Experimental System 3	Control System 3
Acetic acid (mg/L)	3200	500
Lactic acid (mg/L)	1500	150
CODcr (mg/L)	5000	6000

[0191] The biological power generator was supplied with the liquid of smaller molecular weight under treatment (Experimental system 3) or the polymeric substance-containing liquid under treatment (Control system 3), which were passed through the anaerobic region 5a that had been adjusted to a pH of approximately 7; the treated liquid 6 was then discharged through the treated liquid discharge port. Humidified air adjusted to have a relative humidity of 100% was fed into the aerobic region 5b via the air intake port 64; the humidified air passing through the aerobic region 5b was discharged through the exhaust vent 66. An excess alkaline aqueous solution generated in the aerobic region 5b was washed down by flowing a small amount of water with times and then recovered.

[0192] The effective capacity of the apparatus under consideration was 1500 mL for the anaerobic region 5a (microbial reaction compartment) and 500 mL for the aerobic region 5b (air reaction compartment); the feed rate was so adjusted that the liquid under treatment would have a residence time of 15 days and the air a residence time of 1 minute. The total electrode surface was set at 300 cm^2 for both anode and cathode. The experiments were conducted in a constant-temperature bath with 30°C. With the date of the start of normal operation being designated day zero, the anode-cathode voltage and current density, as well as the CODcr concentration and the concentrations of organic acids (acetic acid and lactic acid) in the treated liquid waste were recorded with times; the results are shown in FIG. 14.

[0193] In Experimental system 3, from day zero to day 40 after the start of normal operation, the current density and voltage were stable at approximately 4.0 A/m^2 and 0.4 V, respectively; the CODcr concentration was approximately 350 mg/L on the day normal operation started but it then decreased slowly until it reached approximately 100 mg/L at day 20. A steady state then followed and the value remained stable around 100 mg/L.

[0194] The acetic acid concentration behaved in a similar way to the CODcr concentration; it gradually decreased from 250 mg/L and reached about 80 mg/L at day 20. A steady state then followed and the value remained stable. The lactic acid concentration was approximately about 50 mg/L at the start of normal operation but it gradually decreased to about 20 mg/L at day 20, with a steady state then following.

[0195] Although not shown, the power density per hour (voltage times current divided by electrode area) was approximately about 140 kWh/m^2.

[0196] In Control system 3, on the other hand, the current density continued to decrease very slowly in the period from day zero to day 15 after the start of normal operation, decreasing from about 3.2 A/m^2 to 2.0 A/m^2; thereafter, the value was stable at approximately 2.0 A/m^2. The voltage was stable at approximately 0.3 V throughout the period of normal operation.

[0197] At day zero before the start of normal operation, the CODcr concentration was approximately 800 mg/L but after the start of normal operation, it showed a tendency to increase and rose to about 1600 mg/L at day 7. Thereafter, it increased very slowly and reached approximately 2500 mg/L at day 20, followed by a steady state.

[0198] The acetic and lactic acid concentrations were approximately 300 mg/L and 150 mg/L, respectively, at day zero before the start of normal operation but after the start of normal operation, the organic acids began to be consumed and their concentrations decreased. At day 20 and thereafter, the acid fermenting bacteria began to predominate and the organic acids accumulated to increase until day 40.

[0199] Although not shown, the power density per unit area of electrode (voltage times current divided by electrode area) was about 52-78 kWh/m^2 per hour.

[0200] In Experimental system 3, acid fermentation proceeded adequately in the polymer-degradation vessel 103 (the organic polymeric substances had their molecular weight reduced adequately), so the acid fermenting bacteria (organic polymeric substance decomposing microorganisms) were dominated by the sulfur reducing bacteria (electrode-active microorganisms) in the anaerobic region 5a (COD was converted to an electric current at 60%). In Control system 3, on the other hand, the organic polymeric substances were present at high concentration in the anaerobic region 5a, so the acid fermenting bacteria predominated over the sulfur reducing bacteria; as a result, it could be said that the density of the electric current produced began to decrease immediately after the start of normal operation, and the energy in the COD components was converted to electricity at a lower efficiency than in the Experimental system (COD was converted

to an electric current at an efficiency of 45%).

[0201] Furthermore, in Experimental system 3, the CODcr concentration of the treated water began to decrease immediately after the start of normal operation and dropped to approximately about 120 mg/L in about 10 days. In Control system 3, on the other hand, the CODcr concentration of the treated water began to increase immediately after the start of normal operation and exceeded 2300 mg/L in about 15 days. This shows that the apparatus of the present invention for treating organic polymeric substance-containing wastewater exhibit an extremely high performance in water treatment.

[Examples 4-6]

[0202] The experimental biological power generator shown in FIG. 7 was connected to various types of post-treatment vessel, an aerobic biological treatment vessel (Example 4), the second biological power generator (Example 5), or a batchwise activated sludge vessel (Example 6), and these systems were compared for their performance in water treatment and power generation with the case where no post-treatment was carried out (Control system 4).

<Second biological power generator>

[0203] Except for the anode, the second biological power generator was constructed in the same way as the biological power generator of FIG. 7 and before starting the operation, 20 mL of an electrode-active microorganism enriched culture was added to the anaerobic region.

[0204] Carbon paper (EC-TP1-060 of Electrochem, Inc.) was used as an anode material, and 5-hydroxy-1,4-naphthoquinone (5-H-1,4-NQ) was used as an electron mediator to be immobilized on the anode.

[0205] Five grams of 5-H-1,4-NQ of Aldrich was dissolved in 100 mL of 20% (v/v) chlorosulfonic acid/dichloromethane solution and subjected to reaction for 20 hours at room temperature in the presence of 2 mL of conc. sulfuric acid, whereby sulfonic acid chloride groups were introduced.

[0206] In a separate step, commercial Vulcan XC-72R (Cabot) carbon black was sampled in 10 g and 10 mmol each of sulfanilic acid and a nitrite was allowed to act on the carbon black, whereupon sulfonic acid groups were introduced into it by the diazo coupling reaction. Using oxalyl chloride, the introduced sulfonic acid groups were converted to sulfonyl chloride. Further, in the solvent THF (tetrahydrofuran), 1,3-propanediamine was acted on the carbon black to introduce amino groups into its surface. The density of the amino groups introduced in the resulting aminated carbon black was determined by titration, giving a value of 500 μml/g.

[0207] Twenty grams of the resulting aminated carbon black, 100 mmol of 5-H-1,4-NQ chloride, and 8 mL of triethylamine were subjected to reaction in the solvent DMF (dimethylformamide) at 50°C for 24 hours, and the reaction product was dried. The dried reaction product was dispersed in an isopropanol solution of 5% Nafion (registered trademark), coated on carbon paper (EC-TP1-060 of Electrochem, Inc.), and dried.

[0208] The anode had a standard electrode potential of -0.10 V.

<Water under treatment: Organic pollutant-containing liquid waste>

[0209] The organic pollutant-containing liquid waste was a liquid waste from a food plant having a BOD of 2 g/L that was primarily composed of polysaccharides and which was preliminarily put into a jar fermenter (polymer-degradation vessel) under anaerobic conditions, where it was subjected to a biological treatment for reduction in molecular weight at pH of 5.0-6.0 and 35°C for 48 hours at an agitating speed of 50 rpm. The BOD of the thus prepared influent into the power generator (water under treatment) was stable at about 1.7 g/L.

<Operation of the biological power generator>

[0210] No replacemant of the water-under treatment in the anaerobic region (microbial reaction compartment) was carried out for 10 days after the start of operation so that the microorganisms would adhere to the inside walls of the anaerobic region in the process but, instead, the Desulfuromonas medium (Table 5) described in Handbook of Microbial Media (Atlas et al., 1997, CRC Press) was loaded into the anaerobic region 5a (microbial reaction compartment) so that sulfur-reducing bacteria (electrode-active microorganisms) would become predominant (conditioning). For the subsequent 10 days, a fixing operation was performed with the water under treatment staying for a residence time of 10 days, and starting 20 days after it was started to run, the biological power generator was shifted to normal operation with the water under treatment staying in the anaerobic region for a residence time of 3 days, during which period the amount of current flowing between anode and cathode and the voltage across the two electrodes were measured.

[0211] In Examples 4-6, the cathode and the anode were kept electrically connected at all times including the fixing period and the variable resistor was so adjusted as to produce a maximum amount of electric power.

[0212] The aerobic region 5a was so designed that humidified air adjusted to have a relative humidity of 100% would

be fed into it via the air intake port 67 and that the humidified air passing through each aerobic region 5b would be discharged through the exhaust vent 66. An excess alkaline aqueous solution generated in each aerobic region 5b was washed down by flowing a small amount of water with times.

[0213] The effective capacity of the biological power generator was 1300 mL for the anaerobic region (microbial reaction compartment) 5a and 200 mL for the aerobic region (air reaction compartment) 5b; the feed rate was so adjusted that the water under treatment would have a residence time of 3 days and the air a residence time of 1 minute. The total electrode surface area was set at 300 cm^2 for both anode and cathode. The experiments were conducted in a constant-temperature bath with 30°C.

[Example 4]

[0214] In this Example, the biological power generator 5 constructed in the manner described above and a post-treatment vessel 10 were arranged as shown in FIG. 10 and the treated water 6 emerging from the biological power generator 5 during the fixing operation and normal operation was fed into the post-treatment vessel 310 for post-treatment, thereby affording secondary treated water.

[0215] The aerobic biological treatment vessel as the post-treatment vessel 310 was constructed in the following way. An aeration vessel with an effective capacity of 1 L was fabricated and equipped with an air-diffusing pipe, through which air was passed from the bottom at a speed of 0.3 L/min. The aeration vessel was charged with 0.5 L of a foamed polypropylene filter medium of Atacs (average bead size, 3 cm) as a microorganism carrier, which was held in position with metal gauze so that it would not flow out of the vessel. In addition, a precipitation vessel with an effective capacity of 1 L was installed downstream of the aeration vessel to ensure that only the supernatant water would be discharged as treated water. The aeration vessel was charged with 100 mL of sludge from an aeration tank in a sewage treatment plant and after adding sodium acetate and ammonium chloride in respective amounts of 0.5 g/L and 50 mg/L, aeration was performed for 5 days.

[Example 5]

[0216] In this Example, the biological power generator 5 constructed in the manner described above and a post-treatment vessel 410 were arranged as shown in FIG. 12 and the treated water 6 emerging from the biological power generator 5 during the fixing operation and normal operation was fed into the post-treatment vessel 410 for post-treatment.

[0217] The second biological power generator 410 as the post-treatment vessel was run for the conditioning and fixing operations under conditions that complied with those for the conditioning and fixing operations of the biological power generator 5; the treated water 6 from the biological power generator 5 was passed through the second biological power generator 410 for running it in the fixing and normal operating modes, thereby affording secondary treated water.

[Example 6]

[0218] In this Example, treated water 6 was further treated by a batchwise activated sludge method with the combination of an anaerobic and an aerobic step. The experimental apparatus for implementing the batchwise activated sludge method was a reaction vessel having an effective capacity of 400 mL, which was charged with 300 mL of activated sludge collected from an aeration tank in a sewage treatment plant; using this system, synthetic sewage having the composition shown in Table 12 was conditioned for 2 weeks by an operation based on the following cycles: raw water flowing in for 15 minutes (9.6 mL/min); agitation for 2 hours; agitation and aeration for 4.5 hours; precipitation for 45 minutes; and water and sludge discharged for 30 minutes. After the end of the conditioning operation, the raw water was switched to the treated water and a batchwise operation was performed in the same manner. After holding it in a reservoir, the treated water was fed into the batchwise activated sludge reaction vessel at appropriate times to obtain secondary treated water.

[0219] [Table 12]

Table 12 Composition of Synthetic Sewage (mg/L)

Pepton	200
Glucose	200
Yeast Extract	20
$NaHCO_3$	150
$MgSO_4 \cdot 7H_2O$	150
$CaCl_2 \cdot 7H_2O$	50

(continued)

Pepton	200
NaCl	100
$FeSO_4 \cdot 7H_2O$	0.5
KH_2PO_4 .	52.6

[0220] In Control system 4, the treated water 6 from the biological power generator 5 was collected as such and used as secondary treated water.

<Test>

[0221] Where normal operation was carried out for a period of 30 days, the quality of the secondary treated water stabilized at day 10 onward and the BOD concentration of the secondary treated water, as well as its total phosphorus and ortho-phosphorus concentrations were measured in Examples 4-6 and Control system 4; the results are shown in Table 13.

[0222] [Table 13]

Table 13 Quality of Secondary Treated Water in Examples and Control System

	BOD (mg/L) in secondary treated water treated water	Total phosphorus (mg/L) in secondary treated water treated	Orthophosphorus in secondary water
Example 4 (post-treatment with aerobic filter bed)	11	2.4	1.6
Example 5 (second biological power generator)	67	3.8	1.9
Example 6 (anaerobic-aerobic biological treatment)	12	1.2	0.8
Control system 4 (no post-treatment)	200	4.4	2.1

[0223] In Example 4 where treatment with an aerobic filter bed was performed as a post-treatment step, in Example 5 where the post-treatment step was performed using the second biological power generator, and in Example 6 furnished with the batchwise biological treatment vessel having the anaerobic-aerobic step, the quality of the secondary treated water was such that the BOD was consistently no more than 100 mg/L. On the other hand, in Control system 4 which had no post-treatment step, the BOD of the secondary treated water exceeded 150 mg/L which is the uniform standard for emission (daily average) specified by the Water Pollution Prevention Law. Regarding the total phosphorus and ortho-phosphorus, a significant effectiveness in their removal was recognized in Example 6 furnished with the batchwise biological treatment vessel having the anaerobic-aerobic step.

[0224] During the normal operation of the biological power generator in Examples 4-6, voltage and the amount of an electric current were recorded and the results are shown in Table 14. As for Example 5, the voltage and the amount of an electric current in the second biological power generator as the post-treatment vessel are also listed.

[0225] [Table 14]

Table 14 Electricity Generated in Examples and Control System

	Average amount of current (mA)	Average voltage generated (mV)	Average power generated (mW)
Example 4	66	360	23.8
Example 5 (biological power generator)	64	370	23.7

(continued)

	Average amount of current (mA)	Average voltage generated (mV)	Average power generated (mW)
(second biological power generator)	7	310	2.2
Example 6	68	350	23.8

[0226] In all systems, the power generator produced almost comparable amounts of electricity. In Example 5, power generation was effected using the second biological power generator as the post-treatment vessel, so the amount of electrical power generated by the overall system was about 10% larger than in Examples 4 and 6.

[0227] The above results show that the provision of a post-treatment step in the method of generating electrical power while treating wastewater or other waste that contain organic pollutants contributes to further reducing the pollution load in the treated water.

[Example 7]

[0228] A system that used the experimental biological power generator shown in FIG. 7 and which substituted porous graphite for carbon paper as an electrically conductive substrate for anode was evaluated for its power generating performance with anodes of different potentials.

[0229] The anodes were subjected to the following preliminary treatment: the electrically conductive substrate (porous graphite) was wire-connected to the opposite electrode, with a power supply in between, and immersed in 20% aqueous sulfuric acid and with the graphite serving as anode, electrolytic oxidation reaction was performed at an electrode current density of 30-60 mA/cm^2 for a period from 30 minutes to 1 hour. By this treatment, carboxyl and hydroxyl groups were introduced on the graphite surface. The amount of the carboxyl groups introduced can be deduced by measuring, for example, the consumption of sodium hydrogencarbonate.

[0230] The graphite to which carboxyl groups were introduced was in turn reacted with diamine to introduce amino groups. Specifically, the graphite sheet to which carboxyl groups were introduced was dipped in dichloromethane and oxalyl chloride in an amount about 100 times the mole of the introduced carboxyl groups and a few drops of dimethylformamide were added; then, reaction was carried out at room temperature for approximately 4 hours under agitation to thereby convert the above-mentioned carboxyl groups into an acid chloride. Thereafter, the graphite sheet was washed with dichloromethane, dried and transferred into the solvent tetrahydrofuran. To the solvent, 1,3-propanediamine was added in about 100 moles as described above and reaction was carried out at room temperature for approximately 12 hours under agitation to thereby introduce amino groups. On the graphite to which amino groups were thus introduced, anthraquinone-2,6-disulfonic acid (AQDS, E_0' = -185 mV) (Experimental system 7-1), or Indigo Carmine (E_0' = -125 mV) (Control system 7-1) or 5-hydroxy-1,4-naphthoquinone (5-H-1,4-NQ, E_0' = -3 mV) (Control system 7-2) was immobilized to use the graphite as an anode.

[0231] In other systems, the graphite to which carboxyl groups were introduced was not further treated but 2-methyl-5-amino-1,4-naphthoquinone (2-M-5-A-1,4-NQ) (Experimental system 7-2) or Neutral Red (E_0' = -325 mV) (Control system 7-3) was immobilized to the graphite, which was used as an anode.

[Experimental system 7-1]

[0232] In Experimental system 7-1, AQDS was used after it was converted to a sulfonyl chloride by the following method.

[0233] One mole of AQDS was reacted with 4 moles of sulfolane in 4 moles of the solvent phosphorus oxychloride at 70°C for 24 hours, thereby converting the sulfonic acid groups to a sulfonyl chloride. The product was cooled, filtered, washed first with iced water, then with methanol, and dried to yield a yellow powder of AQDS chloride. The thus prepared AQDS chloride was checked for purity in terms of the size of the sulfonyl chloride peak in FTIR and by elemental analysis.

[0234] The graphite to which amino groups were introduced (electrically conductive substrate) was dipped in tetrahydrofuran and under mild agitation, the AQDS chloride prepared by the method described above was added in an excess amount with respect to the amino groups; in the presence of triethylamine in an amount 5 times the mole of the added sulfonyl chloride, reaction was carried out at room temperature for approximately 12 hours, whereby sulfonamide bonds were formed between the graphite and the electron transfer medium. The product was washed with methanol, reacted with water for 24 hours or more, and then dried to yield an anode for biological power generation.

[0235] To this anode, an electric potential was applied in an aqueous solution at pH 7, with the applied potential being shifted from -0.25 V to -0.15 V (hydrogen standard electrode potential), whereupon an electric current was generated that was by far greater than the static current that would be observed with untreated graphite; hence, one may conclude

that the anode has a standard electrode potential E_0' between -0.25 V and -0.15 V.

[Experimental system 7-2]

[0236] The graphite to which carboxyl groups were introduced was dipped in dimethylformamide and under mild agitation, 2-M-5-A-1,4-NQ was added in an excess amount (more than 100 mol%) with respect to the carboxyl groups; in the presence of dicyclohexyl carbodiimide, reaction was carried out at room temperature for 72 hours, whereby amide bonds were formed between the amino groups in the 2-M-5-A-1,4-NQ and the carboxyl groups on the graphite so that the electron mediator was immobilized on the graphite surface. The product was washed first with dimethylformamide, then with methanol, and dried to prepare an anode for biological power generation.

[0237] To this anode, an electric potential was applied in an aqueous solution at pH 7, with the applied potential being shifted from -0.15 V to -0.13 V (hydrogen standard electrode potential), whereupon an electric current was generated that was by far greater than the static current that would be observed with untreated graphite; hence, one may conclude that the anode has a standard electrode potential E_0' between

- 0.15 V and -0.13 V.

[Control system 7-1]

[0238] In Control system 7-1, Indigo Carmine was used after it was converted to a sulfonyl chloride by the following method.

[0239] One mole of Indigo Carmine was reacted with 4 moles of sulfolane in 4 moles of the solvent phosphorus oxychloride at 70°C for 24 hours, thereby converting the sulfonic acid groups to a sulfonyl chloride. The product was cooled, filtered, washed with iced water and then dried to yield a blue powder of Indigo Carmine chloride.

[0240] The graphite to which amino groups were introduced (electrically conductive substrate) was dipped in tetrahydrofuran and under mild agitation, the above-mentioned Indigo Carmine chloride was added in an excess amount (more than 100 mol%) with respect to the amino groups; in the presence of triethylamine in an amount 5 times the mole of the added Indigo Carmine chloride, reaction was carried out at room temperature for approximately 12 hours, whereby sulfonamide bonds were formed between the amino groups and the Indigo Carmine chloride to introduce an electron mediator. The product was washed with methanol, then washed with water, and dried to yield an anode for biological power generation.

[0241] To this anode, an electric potential was applied in an aqueous solution at pH 7, with the applied potential being shifted from -0.13 V to -0.10 V (hydrogen standard electrode potential), whereupon an electric current was generated that was by far greater than the static current that would be observed with untreated graphite; hence, one may conclude that the anode has a standard electrode potential E_0' between -0.13 V and -0.10 V.

[Control 7-2]

[0242] In Control 7-2, 5-H-1,4-NQ was used after it was converted to a sulfonyl chloride by the following method.

[0243] Five grams of 5-H-1,4-NQ manufactured by Aldrich was dissolved in 100 mL of 20% (v/v) chlorosulfonic acid/dichloromethane solution and reaction was carried out in the presence of 2 mL of conc. sulfuric acid at room temperature for 20 hours, thereby introducing sulfonic acid chloride groups.

[0244] The graphite to which amino groups were introduced (electrically conductive substrate) was dipped in tetrahydrofuran and under mild agitation, the above-mentioned 5-H-1,4-NQ sulfonic acid chloride was added in an excess amount (more than 100 mol%) with respect to the amino groups; in the presence of triethylamine in an amount 5 times the mole of the added 5-H-1,4-NQ sulfonic acid chloride, reaction was carried out at room temperature for approximately 12 hours, whereby sulfonamide bonds were formed between the hydrophilic polymer and 5-H-1,4-NQ to introduce an electron mediator. The product was washed with methanol and dried to yield an anode for biological power generation.

[0245] To this anode, an electric potential was applied in an aqueous solution at pH 7, with the applied potential being shifted from -0.10 V to +0.05 V (hydrogen standard electrode potential), whereupon an electric current was generated that was by far greater than the static current that would be observed with untreated graphite; hence, one may conclude that the anode has a standard electrode potential E_0' between -0.10 V and +0.05 V.

[Control 7-3]

[0246] The graphite to which carboxyl groups were introduced was dipped in dimethylformamide and under mild agitation, Neutral Red was added in an excess amount (more than 100 mol%) with respect to the carboxyl groups; in the presence of dicyclohexyl carbodiimide, reaction was carried out at room temperature for 72 hours, whereby amide

bonds were formed between the amino groups in the Neutral Red and the carboxyl groups on the graphite surface to immobilize the electron mediator. The product was washed first with dimethylformamide, then with methanol, and dried to prepare an anode for biological power generation.

[0247] To this anode, a potential was applied in an aqueous solution at pH 7, with the applied potential being shifted from -0.45 V to -0.28 V (hydrogen standard electrode potential), whereupon an electric current was generated that was by far greater than the static current that would be observed with untreated graphite; hence, one may well conclude that the anode has a standard electrode potential E_0' between -0.45 V and -0.28 V.

<Power generating performance>

[0248] Using the anodes prepared in Experimental systems 7-1 and 7-2, as well as in Control systems 7-1, 7-2 and 7-3, power generation tests were performed with the biological power generator shown in FIG. 7, and the results are shown in

Table 15.

[0249] In Example 7, a model of water-containing organic substance prepared by mixing 0.01 g/L of a yeast extract in 0.1 mol/L of a glucose solution was used as a substrate solution. No replacemant of the liquid in the anaerobic region (biological reaction compartment) was carried out for 10 days after the start of operation so that the organisms would adhere to the inside walls of the anaerobic region in the process but, instead, the above-mentioned Desulfuromonas medium (Table 5) was loaded into the anaerobic region (biological reaction compartment) so that sulfur-reducing bacteria would become predominant. Starting at day 10 after the start of operation, a fixing operation was performed, with the substrate solution staying for a residence time of 2 days, and starting at day 20 after the start of operation, normal operation was performed with the substrate solution staying in the anaerobic region for a residence time of 500 minutes, during which period the amount of current flowing between anode and cathode and the voltage across the two electrodes were measured. Note that air was fed into the aerobic region with a residence time of 0.5 minutes.

[0250] [Table 15]

Table 15 Power Generation Test Results

Experimental system	Electron mediator immobilized on anode	Anode potential E_0' (V)	Average current generated (mA)	Average voltage output (mV)	Average (mW)
Experiment 7-1	AQDS	-0.25--0.15	84	370	31
Experiment 7-2	2-M-5-A-1,4-NQ	-0.15--0.13	41	295	12
Control 7-1	Indigo Carmine	-0.13--0.10	1.2	250	0.3
Control 7-2	5-H-1,4-NQ	-0.10-+0.05	12	240	2.9
Control 7-3	Neutral Red	-0.45--0.28	1.8	380	0.7

[0251] From the results shown in Table 15, it can be seen that in terms of the electrical output produced, the case where the standard electrode potential (E_0') of the anode was within the range of from -0.13 to -0.28 V as claimed by the present invention (Experimental systems) was superior to the case where it was outside the claimed range (Control systems) and produced about 4-100 times more power.

[0252] Comparing Experimental systems 7-1 and 7-2, the former displayed about 2.6 times more output than the latter; this would be because the standard electrode potential of the anode in Experimental system 7-1 was within the range of -0.25 to -0.15 V whereas that of the anode in Experimental system 7-2 was in a somewhat higher range of -0.15 to -0.13 V. From these results, it can be seen that from the viewpoint of power generating performance, it is advantageous for the standard electrode potential of anode at pH 7 to be set within the range from -0.13 to -0.28 V, preferably within the range from -0.15 V to -0.27 V.

INDUSTRIAL APPLICABILITY

[0253] The present invention, if applied to the treatment of organic wastewater and waste containing organic pollutants, as exemplified by wastewater, liquid waste, night soil, food waste and sludge, can produce electrical energy efficiently

while treating wastewater or waste that contain organic polymeric substances.

Claims

1. A biological power generator comprising:

   an anaerobic region containing microorganisms capable of growth under anaerobic conditions and an anode having an electron mediator immobilized thereon and having a standard electrode potential (E_0') in the range of -0.13 V to -0.28 V at pH 7;
   an aerobic region containing molecular oxygen and a cathode; and
   a diaphragm that defines the anaerobic region and the aerobic region.

2. The biological power generator according to claim 1, wherein the anode having an electron mediator immobilized thereon is such that at least one electron mediator selected from the group consisting of anthraquinone derivatives, naphthoquinone derivatives, benzoquinone derivatives, and isoalloxazine derivatives is immobilized on an electrode substrate.

3. The biological power generator according to claim 2, wherein the electron mediator is at least one species selected from the group consisting of anthraquinone carboxylic acids (AQC), aminoanthraquinones (AAQ), diaminoanthraquinones (DAAQ), anthraquinone sulfonic acids (AQS), diaminoanthraquinone sulfonic acids (DAAQS), anthraquinone disulfonic acids (AQDS), diaminoanthraquinone disulfonic acids (DAAQ DS), ethyl anthraquinones (EAQ), methyl naphtoquinones (MNQ), methyl aminonaphtoquinones (MANQ), bromomethyl aminonaphtoquinones (BrMANQ), dimethyl naphtoquinones (DMNQ), dimethyl aminonaphtoquinones (DMANQ), lapachol (LpQ), hydroxy(methylbutenyl)aminonaphthoquinones (AlpQ), naphthoquinone sulfonic acids (NQS), trimethyl aminobenzoquinones (TMABQ), flavin mononucleotide (FMN), and derivatives thereof.

4. A method of treating organic waste by making use of the biological power generator according to any one of claims 1-3.

5. A method of treating organic solid pollutant-containing waste by making use of a biological power generator comprising an anaerobic region containing microorganisms capable of growth under anaerobic conditions and an anode having an electron mediator immobilized thereon and having a standard electrode potential (E_0') in the range of -0.13 V to -0.28 V at pH 7, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region, **characterized by** comprising:

   a solubilizing step in which the organic solid pollutants in the organic solid pollutant-containing waste are solubilized to form a liquid under treatment which contains solubilized organic substances (a solubilized liquid under treatment); and
   a biological power generation step in which the solubilized liquid under treatment is fed into the anaerobic region of the biological power generator so that the oxidation reaction by the microorganisms which use the solubilized organic substances within the anaerobic region as an electron donor, and the reduction reaction which uses the oxygen within the aerobic region as an electron acceptor are allowed to proceed to thereby reduce a pollution load in the solubilized liquid under treatment while generating electricity.

6. The method of treating organic solid pollutant-containing waste according to claim 5, which is **characterized in that** the solubilizing step is performed by at least one method selected from among mechanical crushing, ultrasonic crushing, thermal treatment, hydrothermal electrolytic treatment, acid or alkali treatment, and oxidizing treatment.

7. An apparatus for treating organic solid pollutant-containing waste, **characterized by** comprising:

   a solubilizing vessel in which the organic solid pollutants in the organic solid pollutant-containing waste are solubilized to form a liquid under treatment which contains solubilized organic substances (a solubilized liquid under treatment); and
   a biological power generator comprising an anaerobic region that is furnished with a liquid-under-treatment receiving inlet for receiving the solubilized liquid under treatment and which contains microorganisms capable of growth under anaerobic conditions and an anode having an electron mediator immobilized thereon, and having a standard electrode potential (E_0') in a range of -0.13 V to -0.28 V at pH 7, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region.

8. A method of treating organic polymeric substance-containing wastewater by making use of a biological power generator comprising an anaerobic region containing microorganisms capable of growth under anaerobic conditions and an anode having an electron mediator immobilized thereon and having a standard electrode potential (E_0') in a range of -0.13 V to -0.28 V at pH 7, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region, **characterized by** comprising:

a polymer-degradation step in which the organic polymeric substances in the organic polymeric substance-containing liquid waste are reduced in molecular weight to form a liquid under treatment which contains organic substances reduced in molecular weight (a liquid of smaller molecular weight under treatment); and
a biological power generation step in which the liquid of smaller molecular weight under treatment is fed into the anaerobic region of the biological power generator so that the oxidation reaction by the electrode-active microorganisms which use the organic substances reduced in molecular weight within the anaerobic region as an electron donor and the reduction reaction which uses the oxygen within the aerobic region as an electron acceptor are allowed to proceed to thereby reduce a pollution load in the liquid of smaller molecular weight under treatment while generating electricity.

9. The method of treating organic polymeric substance-containing wastewater according to claim 8, **characterized in that** in the polymer-degradation step, the organic polymeric substances are reduced in molecular weight by a biological treatment that makes use of the metabolic reaction of anaerobic microorganisms or by an enzymatic reaction that makes use of the decomposition reaction by an enzyme.

10. The method of treating organic polymeric substance-containing wastewater according to claim 9, **characterized in that** in the polymer-degradation step, the organic polymeric substances are reduced in molecular weight to become mainly volatile organic acids.

11. The method of treating organic polymeric substance-containing wastewater according to any one of claims 8-10, **characterized in that** in the polymer-degradation step, the pH of the organic polymeric substance-containing liquid waste is controlled to be within a range of 4.0 to 6.5.

12. The method of treating organic polymeric substance-containing wastewater according to claim 11, **characterized in that** in the polymer-degradation step, the pH of the organic polymeric substance-containing liquid waste is controlled by recovering an alkaline solution from the aerobic region of the biological power generator and feeding the recovered alkaline solution into the anaerobic region.

13. An apparatus for treating organic polymeric substance-containing wastewater which comprises:

a polymer-degradation vessel in which the organic polymeric substances in the organic polymeric substance-containing waste are reduced in molecular weight to form a liquid of a smaller molecular weight under treatment which contains the organic substances that have been reduced in molecular weight (a liquid under treatment of a smaller molecular weight); and
a biological power generator comprising an anaerobic region that is furnished with a liquid-under-treatment receiving inlet for receiving the liquid of smaller molecular weight under treatment and which contains microorganisms capable of growth under anaerobic conditions and an anode having an electron mediator immobilized thereon and having a standard electrode potential (E_0') in the range of -0.13 V to -0.28 V at pH 7, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region.

14. The apparatus for treating organic polymeric substance-containing wastewater according to claim 13, which further includes:

an alkaline solution recovery vessel which recovers an alkaline solution from the aerobic region; and
an alkaline solution supply mechanism for feeding the recovered alkaline solution into the polymer-degradation vessel.

15. A method of treating organic pollutant-containing wastewater by making use of a biological power generator comprising an anaerobic region containing microorganisms capable of growth under anaerobic conditions and an anode having an electron mediator immobilized thereon and having a standard electrode potential (E_0') in the range of -0.13 V to -0.28 V at pH 7, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that

defines the anaerobic region and the aerobic region, which comprises:

a biological power generation step in which the organic pollutant-containing liquid waste is fed into the anaerobic region of the biological power generator so that the oxidation reaction by the microorganisms which use the organic pollutants within the anaerobic region as an electron donor and the reduction reaction which uses the oxygen within the aerobic region as an electron acceptor are allowed to proceed to thereby reduce a pollution load in the organic pollutant-containing liquid waste while generating electricity;
and a post-treatment step in which the pollution load in the treated water as obtained by the biological power generation step is further reduced.

16. The method of treating organic pollutant-containing wastewater according to claim 15, wherein the pollution load is evaluated by at least one index selected from among BOD (biochemical oxygen demand), COD (chemical oxygen demand), nitrogen concentration, and phosphorus concentration.

17. The method of treating organic pollutant-containing wastewater according to claim 15 or 16, wherein the post-treatment step is at least one of the group consisting of a flocculation and precipitation step, a filtering step through activated carbon, a decomposition treatment step by means of aerobic microorganisms, a decomposition treatment step by means of anaerobic microorganisms, a denitrification step, a phosphate removal step, an acid decomposing step, and an oxidation and reduction treatment step by means of electrode-active microorganisms.

18. The method of treating organic pollutant-containing wastewater according to claim 15 or 16, wherein the post-treatment step is an oxidation and reduction treatment step by means of electrode-active microorganisms, in which the treated water from the biological power generator is fed into the anaerobic region and both the oxidation reaction of microorganisms that use the organic substances in the treated water in the anaerobic region as an electron donor and the reduction reaction that uses the oxygen in the aerobic region as an electron acceptor are allowed to proceed, thereby reducing the pollution load in the treated water.

19. The method of treating organic pollutant-containing wastewater according to claim 18, wherein the oxidation and reduction treatment step by means of electrode-active microorganisms as the post-treatment step uses a second anode having a higher standard electrode potential than the anode used in the biological power generation step.

20. An apparatus for treating organic pollutant-containing wastewater which comprises:

a biological power generator comprising an anaerobic region containing microorganisms capable of growth under anaerobic conditions and an anode having an electron mediator immobilized thereon and having a standard electrode potential (E_0') in the range of -0.13 V to -0.28 V at pH 7, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region; and
a post-treatment vessel for further reducing a pollution load in the treated water from the biological power generator.

21. The apparatus for treating organic pollutant-containing wastewater according to claim 20, wherein the post-treatment vessel is at least one of the group consisting of a flocculation and precipitation vessel, an activated carbon assisted filtering vessel, a vessel for decomposition treatment by aerobic microorganisms, a vessel for decomposition treatment by anaerobic microorganisms, a denitrification vessel, a dephosphorylation vessel, an acid decomposing vessel, and a biological power generating vessel.

22. The apparatus for treating organic pollutant-containing wastewater according to claim 20, wherein the post-treatment vessel is a second biological power generator comprising an anaerobic region containing electrode-active microorganisms and an anode having an electron mediator immobilized thereon, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region.

23. The apparatus for treating organic pollutant-containing wastewater according to claim 20, wherein the post-treatment vessel is a second biological power generator comprising an anaerobic region containing electrode-active microorganisms and a second anode having an electron mediator immobilized thereon and having a higher standard electrode potential than the anode having an electrode mediator immobilized thereon in the biological power generator, an aerobic region containing molecular oxygen and a cathode, and a diaphragm that defines the anaerobic region and the aerobic region.

24. The apparatus for treating organic pollutant-containing wastewater according to claim 22 or 23, wherein the electron mediator immobilized on the anode in the power generator is at least one species selected from the group consisting of anthraquinone derivatives, naphthoquinone derivatives, benzoquinone derivatives, and isoalloxazine derivatives; and

the electron mediator immobilized on the anode in the second biological power generator is at least one species selected from the group consisting of anthraquinone derivatives, naphthoquinone derivatives, benzoquinone derivatives, isoalloxazine derivatives, ubiquinone derivatives, cytochrome derivatives, and iron-rich smectite derivatives.

25. The apparatus for treating organic pollutant-containing wastewater according to claim 22 or 23, wherein the electron mediator immobilized on the anode in the power generator is at least one species selected from the group consisting of anthraquinone carboxylic acids (AQC), aminoanthraquinones (AAQ), diaminoanthraquinones (DAAQ), anthraquinone sulfonic acids (AQS), diaminoanthraquinone sulfonic acids (DAAQS), anthraquinone disulfonic acids (AQDS), diaminoanthraquinone disulfonic acids (DAAQ DS), ethyl anthraquinones (EAQ), methyl naphtoquinones (MNQ), methyl aminonaphtoquinones (MANQ), bromomethyl aminonaphtoquinones (BrMANQ), dimethyl naphtoquinones (DMNQ), dimethyl aminonaphtoquinones (DMANQ), lapachol (LpQ), hydroxy(methylbutenyl)aminonaphthoquinones (AlpQ), naphthoquinone sulfonic acids (NQS), trimethyl aminobenzoquinones (TMABQ), flavin mononucleotide (FMN), and derivatives thereof; and

the electron mediator immobilized on the anode in the second biological power generator is at least one species selected from the group consisting of anthraquinone carboxylic acids (AQC), aminoanthraquinones (AAQ), diaminoanthraquinones (DAAQ), anthraquinone sulfonic acids (AQS), diaminoanthraquinone sulfonic acids (DAAQS), anthraquinone disulfonic acids (AQDS), diaminoanthraquinone disulfonic acids (DAAQ DS), ethyl anthraquinones (EAQ), methyl naphtoquinones (MNQ), methyl aminonaphtoquinones (MANQ), bromomethyl aminonaphtoquinones (BrMANQ), dimethyl naphtoquinones (DMNQ), dimethyl aminonaphtoquinones (DMANQ), lapachol (LpQ), hydroxy (methylbutenyl)aminonaphthoquinones (AlpQ), naphthoquinone sulfonic acids (NQS), trimethyl aminobenzoquinones (TMABQ), flavin mononucleotide (FMN), ubiquinone (UQ), 1,4-benzoquinone (1,4-BQ), cytochrome *a*, cytrochrome *b*, cytochrome *c*, nontronite, and derivatives thereof.

26. The apparatus for treating organic pollutant-containing wastewater according to claim 22 or 23, wherein the anode and cathode are directly wire-connected to form a closed circuit in the second biological power generator.

FIG. 1

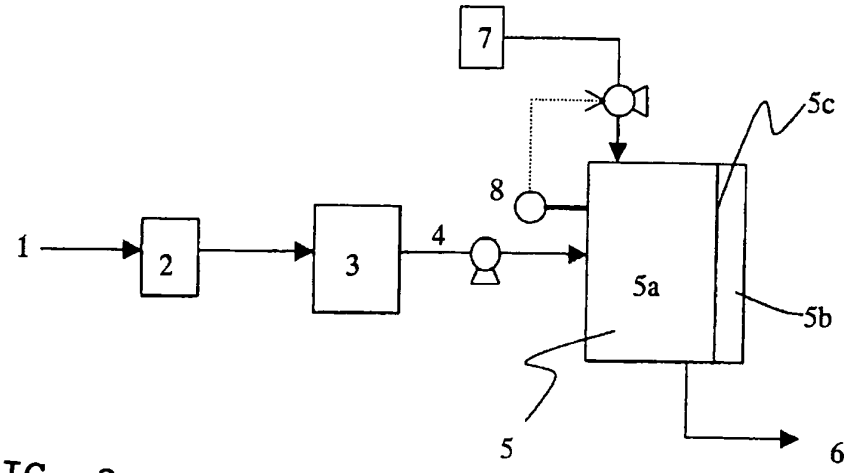


FIG. 2

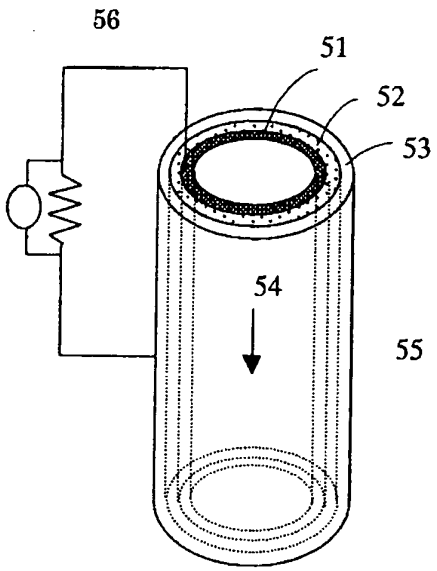


FIG. 3

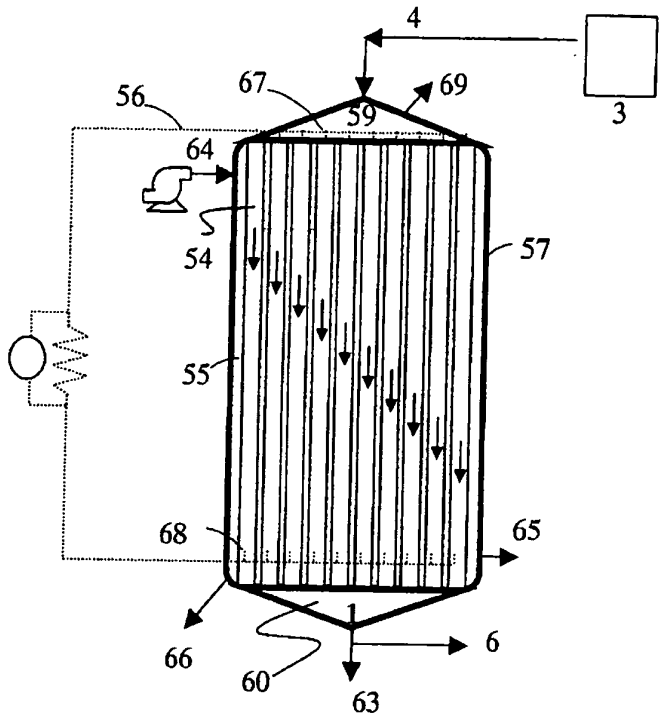


FIG. 4

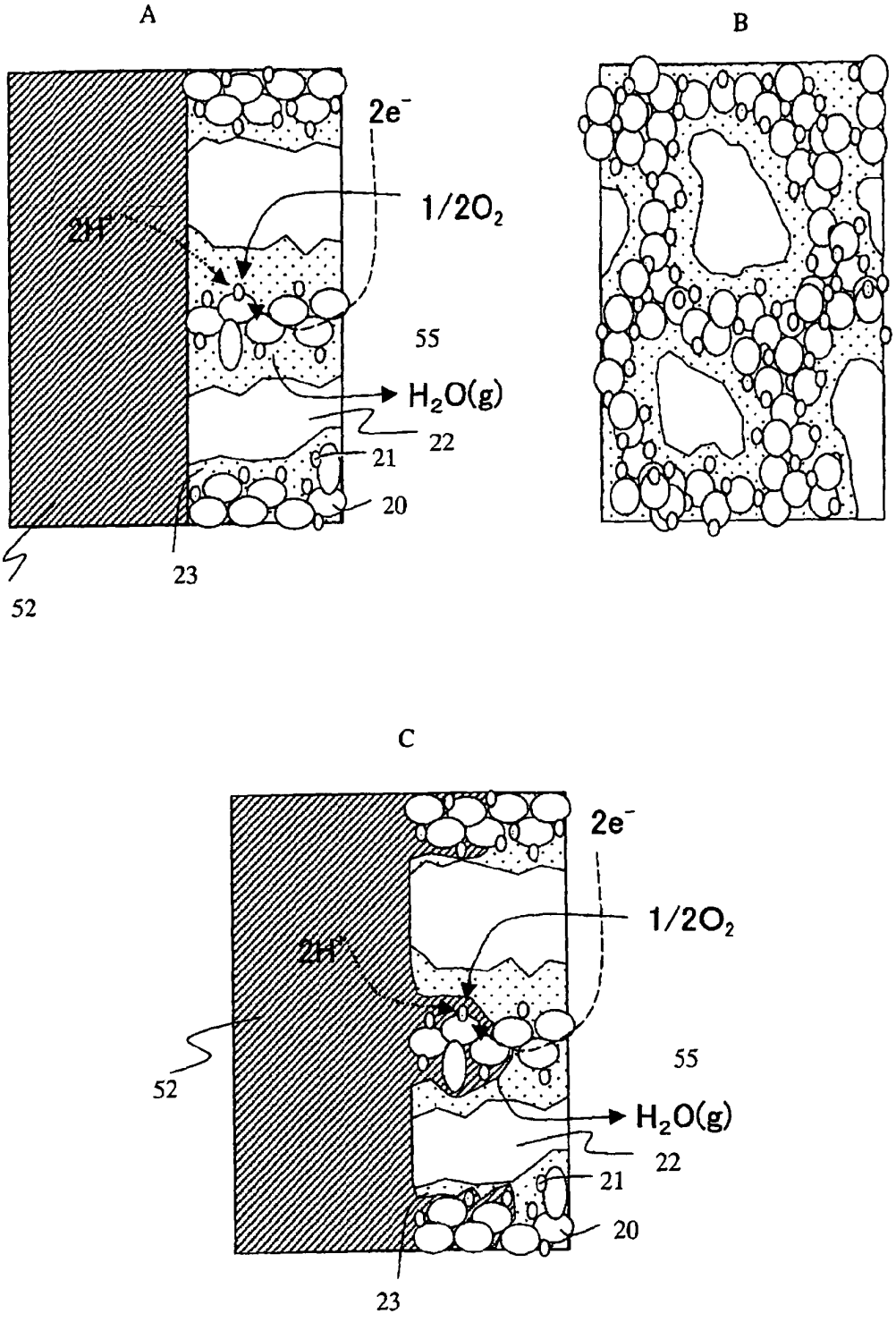


FIG. 5

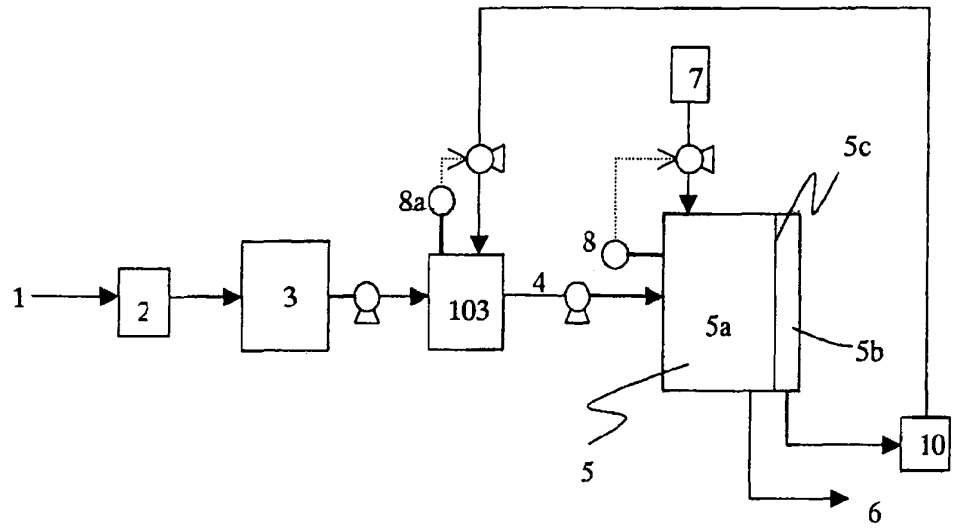


FIG. 6

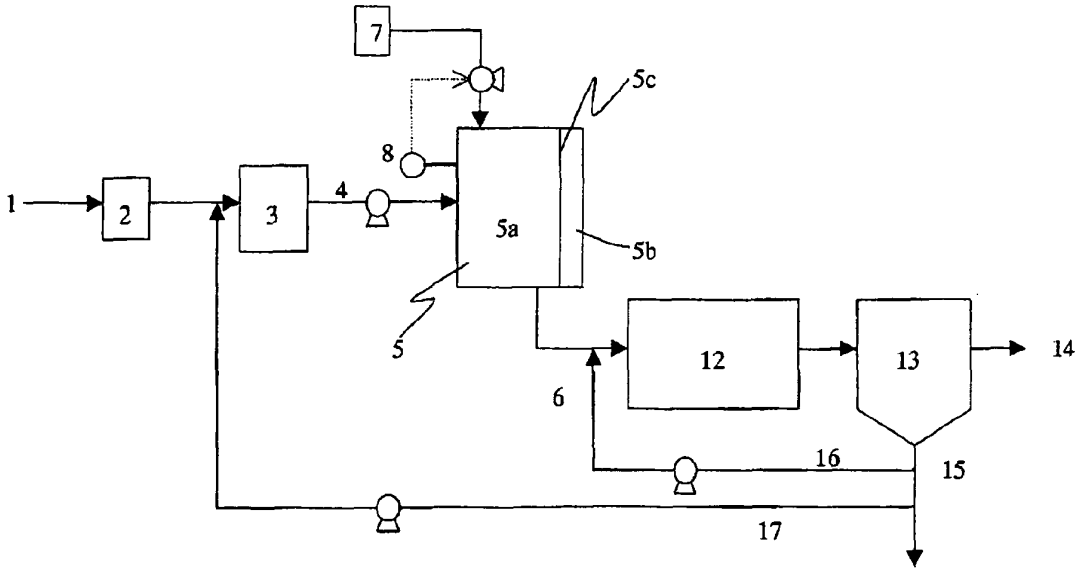


FIG. 7

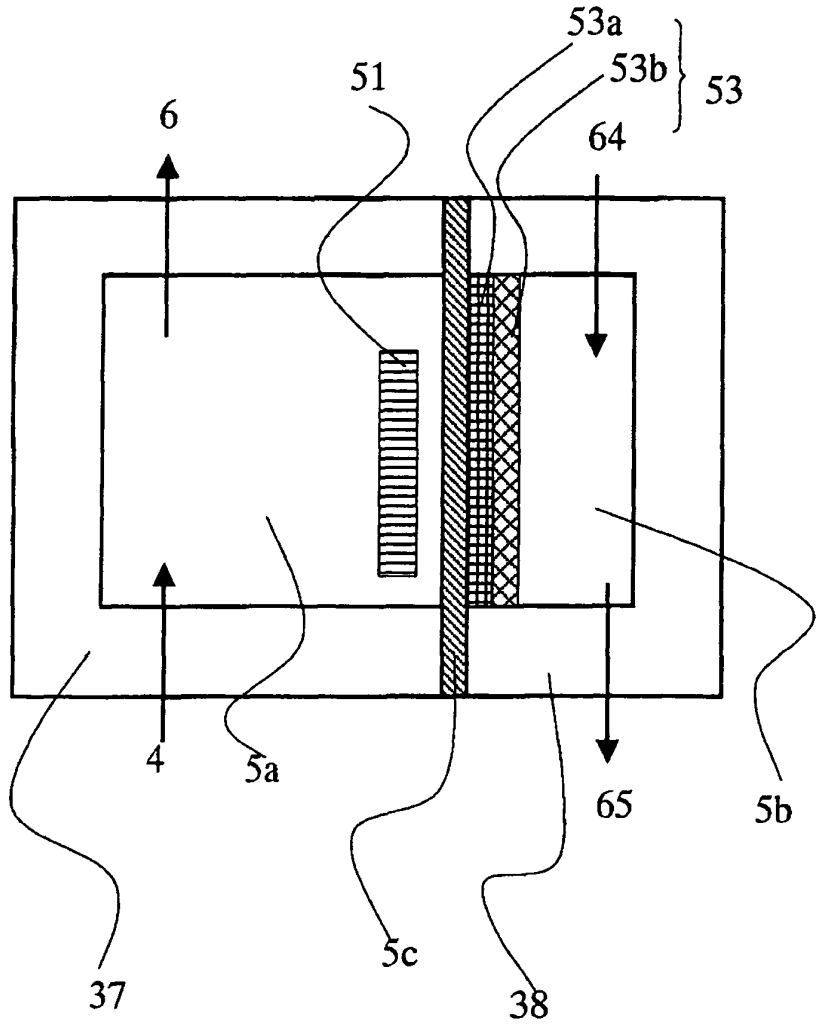


FIG. 8

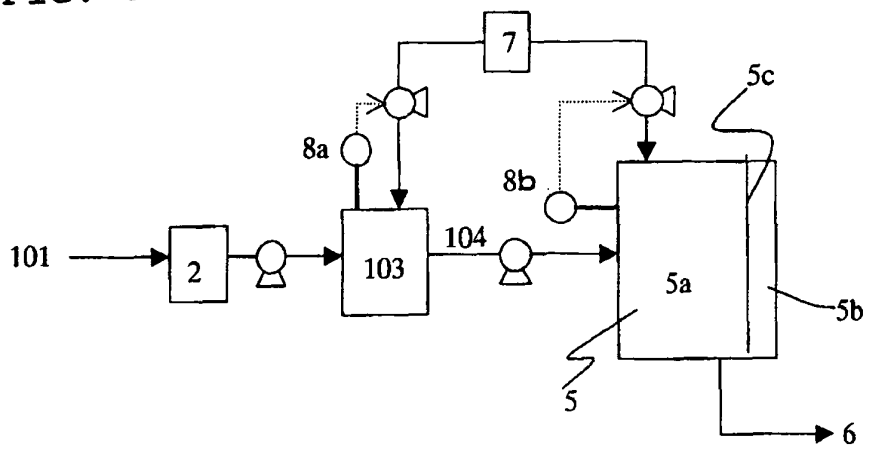


FIG. 9

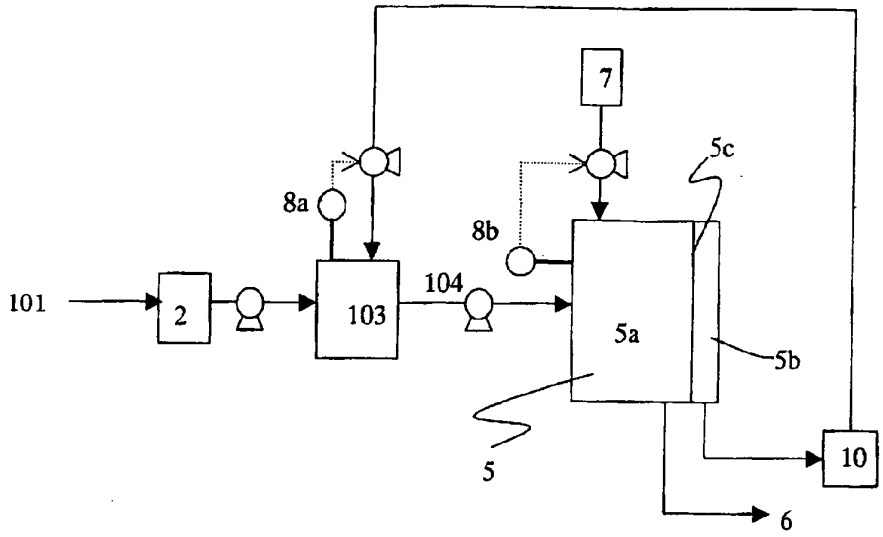


FIG. 10

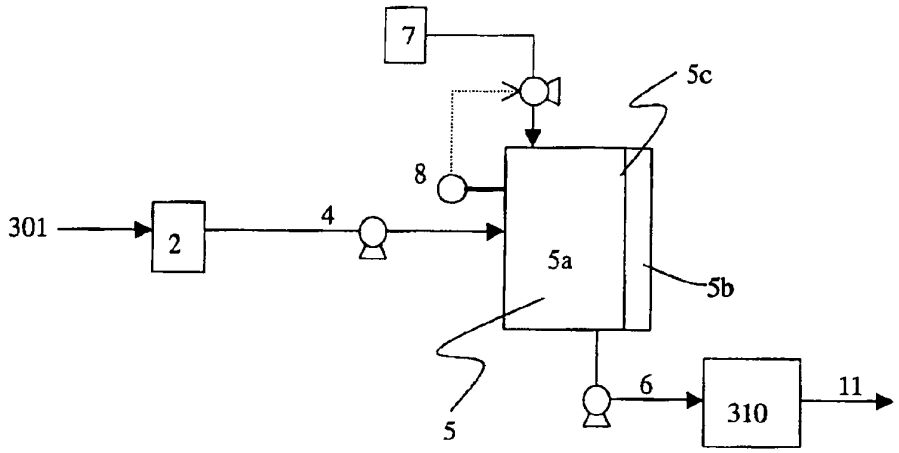


FIG. 11

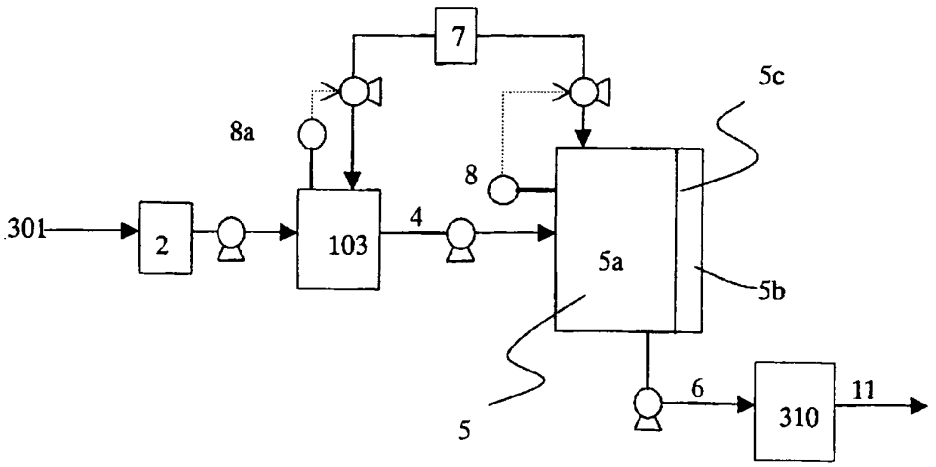


FIG. 12

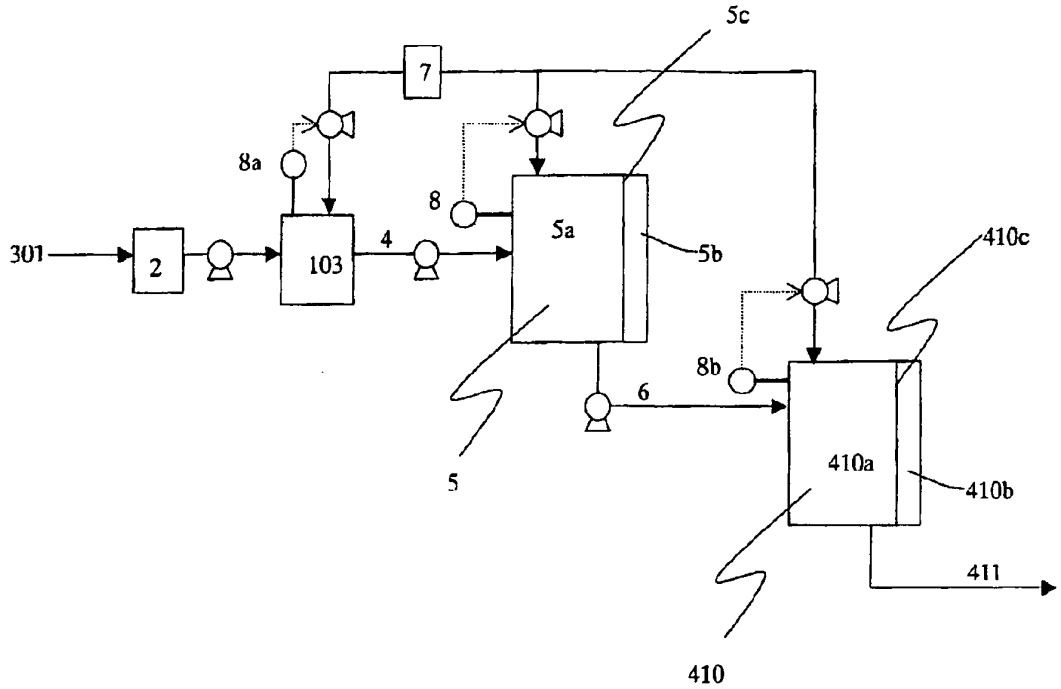
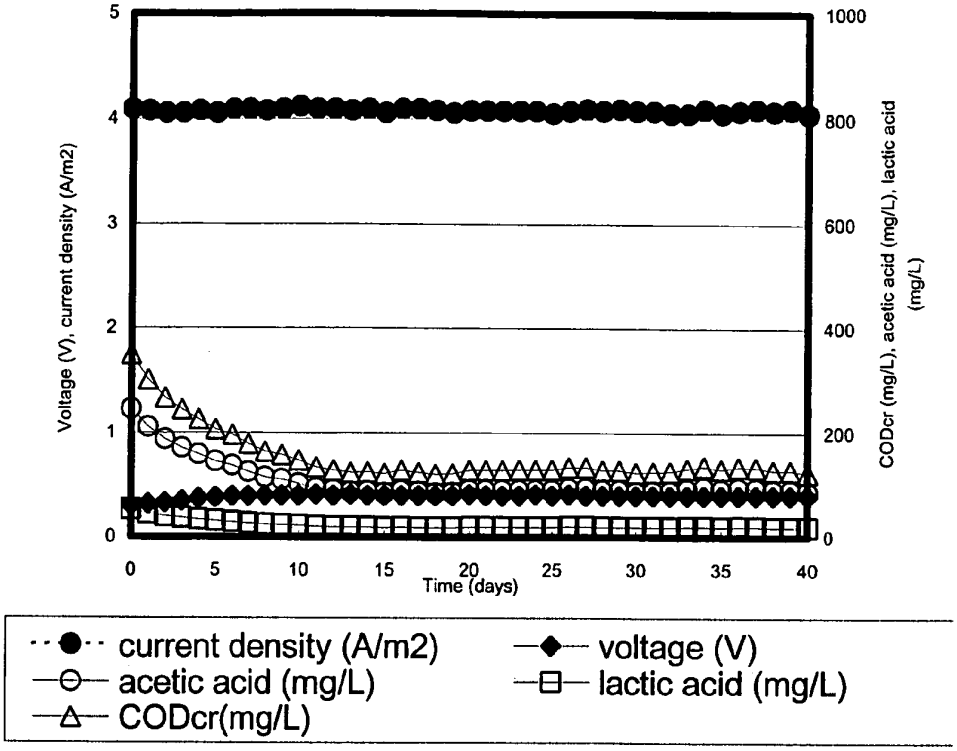
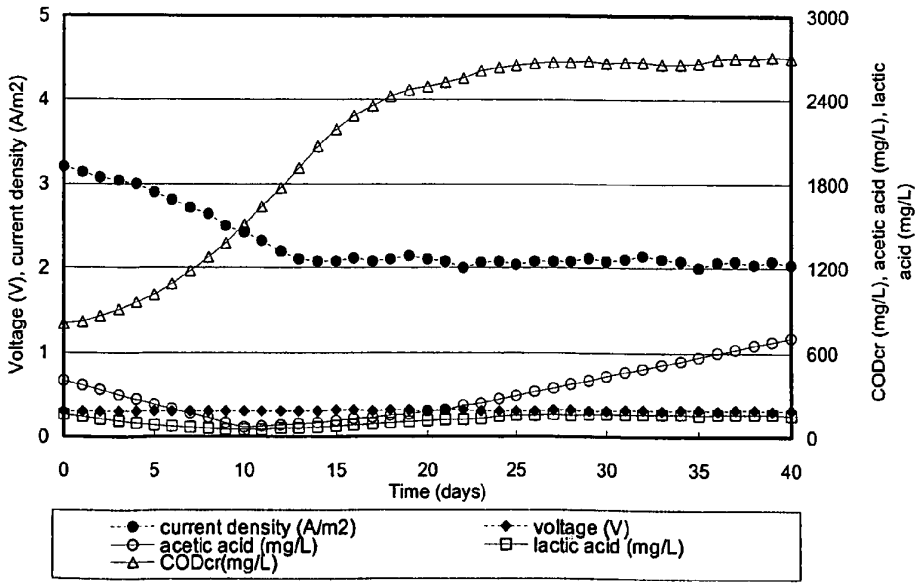


FIG. 13

Experimental Systems



Control Systems



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2006/319152

A. CLASSIFICATION OF SUBJECT MATTER
H01M8/16(2006.01)i, *B09B3/00*(2006.01)i, *C02F11/00*(2006.01)i, *C02F11/02*(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)
H01M8/16, B09B3/00, C02F11/00, C02F11/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2006
Kokai Jitsuyo Shinan Koho 1971-2006 Toroku Jitsuyo Shinan Koho 1994-2006

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2004-342412 A (Ebara Corp.), 02 December, 2004 (02.12.04), Claims; examples (Family: none)	1-26
A	JP 2004-517437 A (Korea Institute of Science and Technology), 10 June, 2004 (10.06.04), Full text & EP 1232123 A & WO 2001/004061 A1	1-26
A	JP 2000-133297 A (Canon Inc.), 12 May, 2000 (12.05.00), Full text (Family: none)	1-26

☒ 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	Date of mailing of the international search report
20 November, 2006 (20.11.06)	28 November, 2006 (28.11.06)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2006/319152

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	JP 2006-81963 A (Hitachi Kiden Kogyo, Ltd.), 30 March, 2006 (30.03.06), Full text (Family: none)	1-26
P,A	JP 2006-66284 A (Hitachi Kiden Kogyo, Ltd.), 09 March, 2006 (09.03.06), Full text (Family: none)	1-26

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 2000133327 A **[0014]**
- JP 2000133326 A **[0014]**
- JP 2002520032 A **[0014]**
- US 4652501 A **[0014]**
- JP 57069667 A **[0014]**
- JP 3022431 B **[0014]**
- WO 9907641 A **[0045]**
- JP 2003290740 A **[0045]**

Non-patent literature cited in the description

- **ROLLER et al.** *Journal of Chemical Technology and Biotechnology,* 1984, vol. 34B, 3-12 **[0014]**
- **BOND et al.** *SCIENCE,* 2002, vol. 295, 483-485 **[0014]**
- **PARK et al.** *Biotechnology Letters,* 2000, vol. 22, 1301-1304 **[0014]**
- **ATSUHARU IKEDA.** Book of Abstracts for the 31st Seminar on New Ceramics. 2004 **[0014]**

US 20130256149A1

(19) **United States**

(12) **Patent Application Publication**

Popat et al.

(10) **Pub. No.: US 2013/0256149 A1**

(43) **Pub. Date: Oct. 3, 2013**

(54) **MICROBIAL ELECTROLYSIS CELLS AND METHODS FOR THE PRODUCTION OF CHEMICAL PRODUCTS**

(71) Applicant: **ARIZONA SCIENCE AND TECHNOLOGY ENTERPRISES LLC**, Scottsdale, AZ (US)

(72) Inventors: **Sudeep Popat**, Chandler, AZ (US); **Prathap Parameswaran**, Tempe, AZ (US); **Cesar Torres**, Tempe, AZ (US); **Bruce Rittmann**, Tempe, AZ (US)

(73) Assignee: **Arizona Science and Technology Enterprises LLC**, Scottsdale, AZ (US)

(21) Appl. No.: **13/839,154**

(22) Filed: **Mar. 15, 2013**

Related U.S. Application Data

(60) Provisional application No. 61/616,893, filed on Mar. 28, 2012.

Publication Classification

(51) **Int. Cl.**

C02F 3/00 (2006.01)

C25B 1/10 (2006.01)

(52) **U.S. Cl.**

CPC .. ***C02F 3/005*** (2013.01); ***C25B 1/10*** (2013.01)

USPC **205/347**; 204/260; 204/253; 205/637; 205/351; 205/638; 205/510

(57) **ABSTRACT**

A microbial electrolysis cell having a brush anode is described. A method of producing products, such as hydrogen, at the cathode of the microbial electrolysis cell is also provided. The microbial electrolysis cell is configured in a cylindrical shape having an anode, cathode and anion exchange membrane all disposed concentrically. A brush anode spirally wound around the outside of the cylindrical microbial electrolysis cell is described. The method may include sparging the anode and/or cathode with air in some cases. In addition, CO_2-containing gas may be injected into a cathode chamber to reduce pH is some cases.

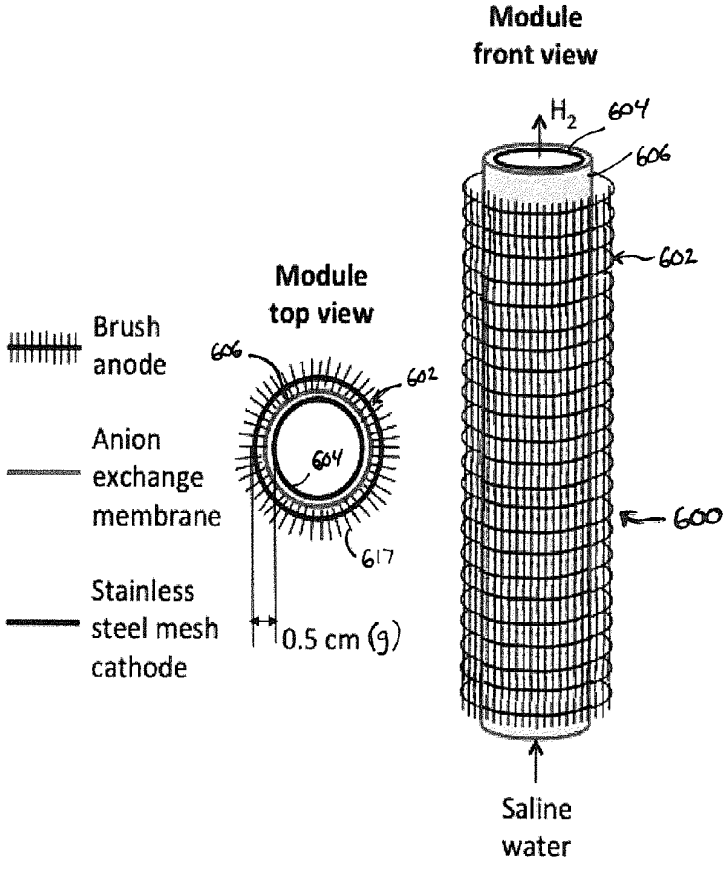


FIG. 6

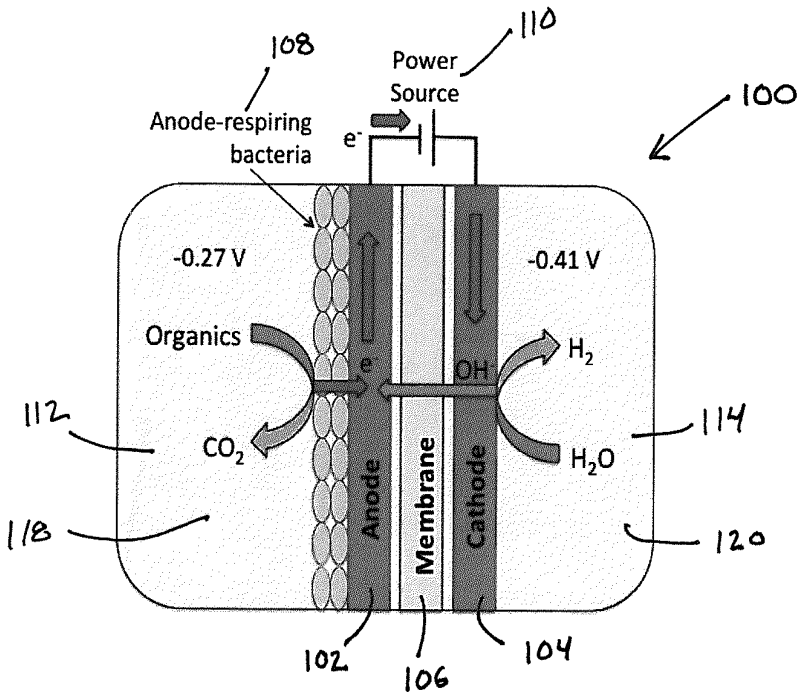

108
110
Power Source
100
Anode-respiring bacteria
e-
-0.27 V
-0.41 V
Organics
e
OH
H2
112
CO2
114
H2O
Anode
Membrane
Cathode
118
120
102
106
104

FIG. 1

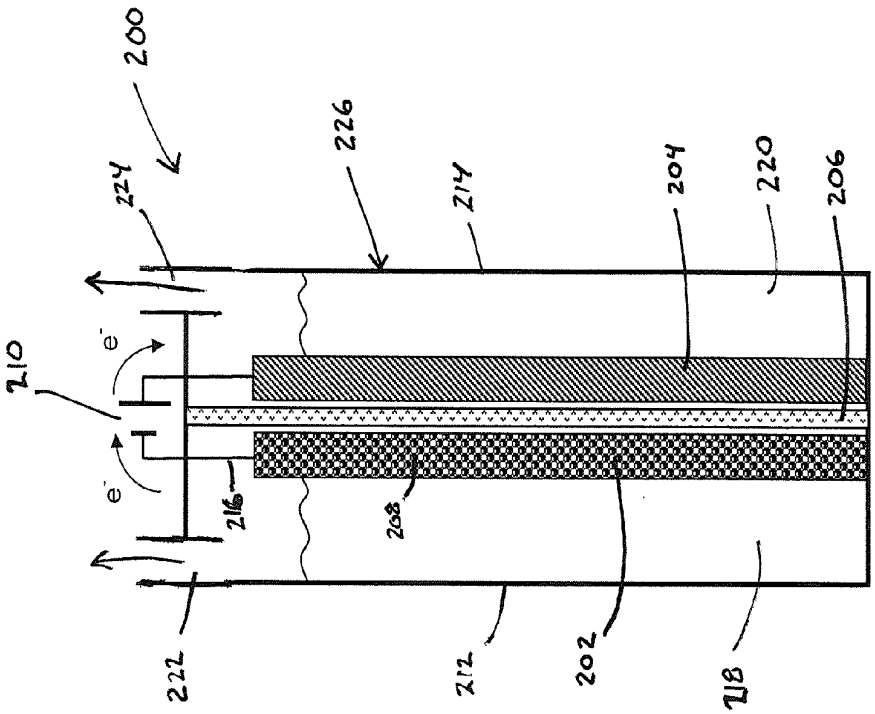


Fig. 2

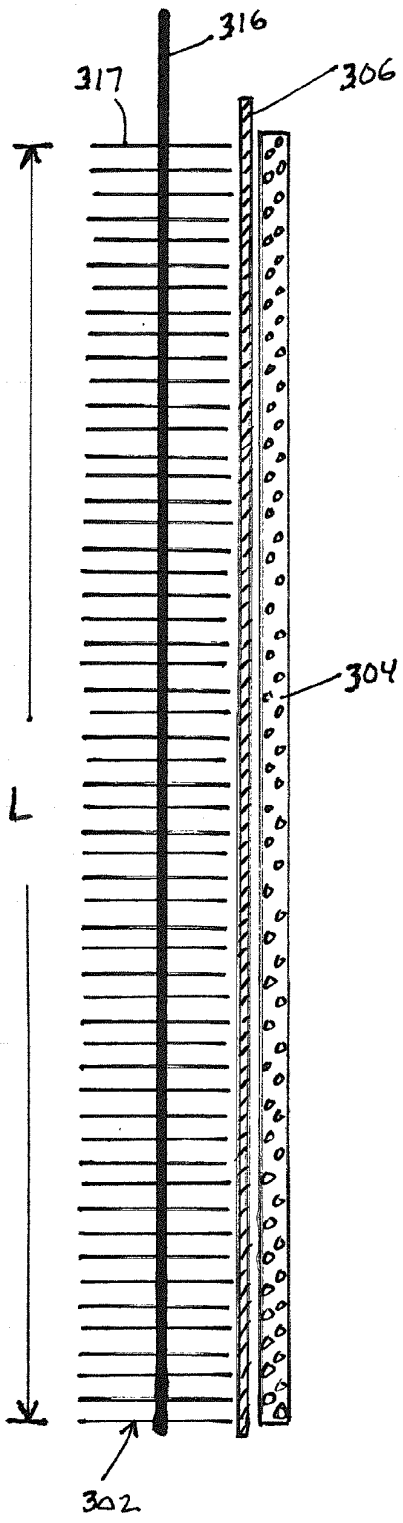


Fig. 3

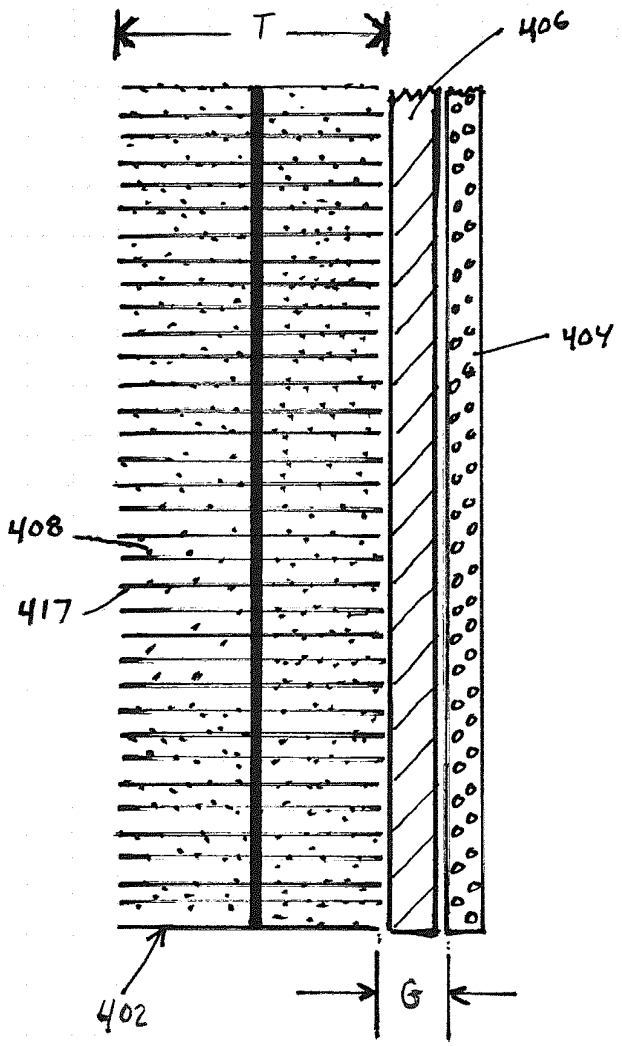


Fig. 4

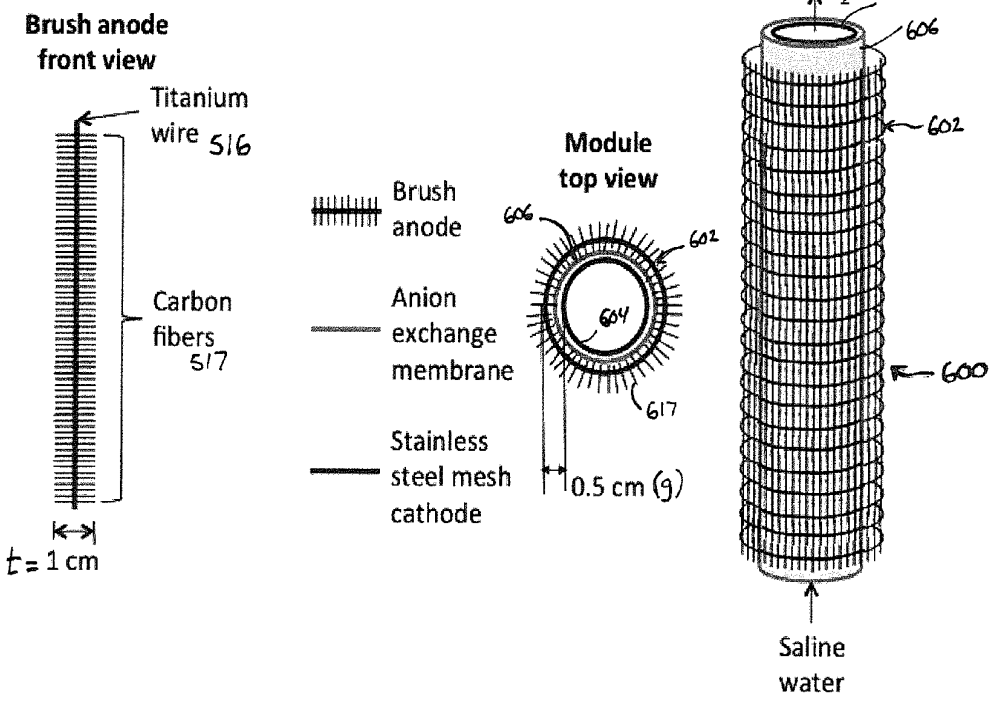

Brush anode
front view
Titanium
wire 516
Carbon
fibers
517
t = 1 cm
Brush
anode
Anion
exchange
membrane
Stainless
steel mesh
cathode
Module
top view
606
602
604
617
0.5 cm (g)
Module
front view
H2
604
606
602
600
Saline
water

FIG. 5

FIG. 6

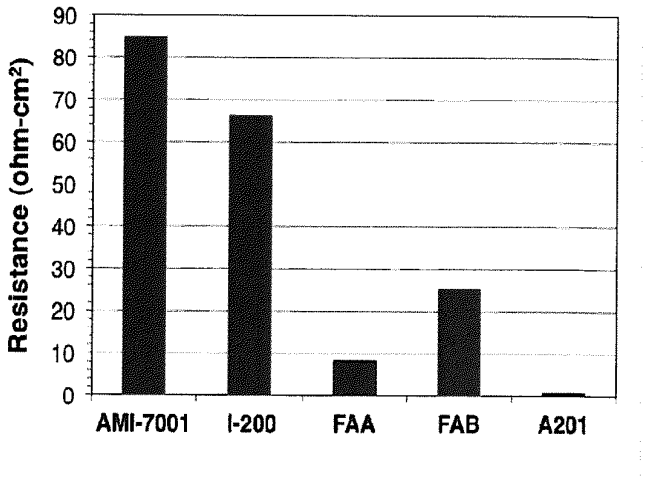

Resistance (ohm-cm²)
90
80
70
60
50
40
30
20
10
0
AMI-7001
I-200
FAA
FAB
A201

FIG. 7

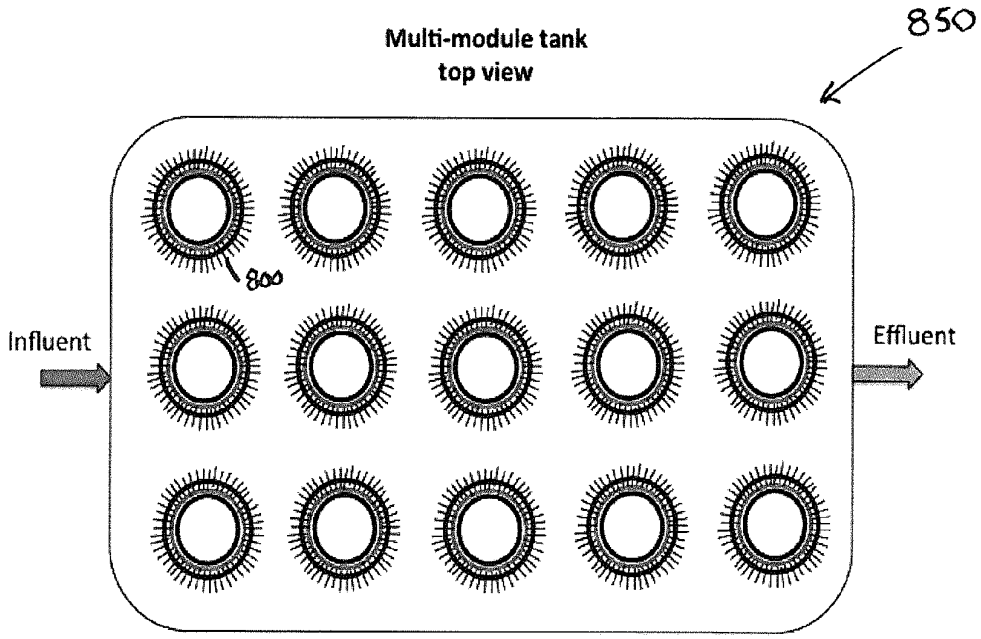


FIG. 8

MICROBIAL ELECTROLYSIS CELLS AND METHODS FOR THE PRODUCTION OF CHEMICAL PRODUCTS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 61/616,893, filed Mar. 28, 2012, entitled "MICROBIAL ELECTROLYSIS CELLS AND METHODS FOR THE PRODUCTION OF CHEMICAL PRODUCTS", which is incorporated herein by reference in its entirety.

FIELD

[0002] This disclosure relates to the field of Microbial Electrolysis Cells (MEGs), including MECs that may be utilized to produce useful chemical products, such as hydrogen gas or caustic soda.

BACKGROUND

[0003] Wastewater from industrial and domestic sources typically contains dissolved organics that need to be removed before the water can be reused. Traditionally, this has been done by aerobic biological treatment. However, this treatment method requires aeration, which consumes large amounts of energy and thus it is an energy intensive process.

[0004] Although wastewater is typically thought of as a nuisance, it is being increasingly recognized as a resource for the production of energy, fuels, and chemicals. While anaerobic digestion has already developed into a mature technology for conversion of wastewater organics to the energetic gas methane (CH_4), not all of the energy extracted from wastewater is available for use, as there are significant losses associated with the conversion of methane to easily usable energy forms such as electricity.

[0005] Recently, a new technology referred to as Microbial Electrolysis Cells (MEC) has gained significant attention with respect to sustainable wastewater treatment. This technology relies on specialized bacteria called anode-respiring bacteria (ARB) that oxidize wastewater organics and transfer electrons thus extracted to an anode. These electrons move through a circuit to a cathode, where water (H_2O) is reduced to produce hydrogen (H_2) gas by applying additional voltage. The MEC is especially attractive since the produced H_2 gas has higher energetic value than CH_4 gas, can be readily converted to useful electrical power using chemical fuel cells, and is a major feedstock to the chemical and petrochemical industries. Other chemical products may be produced, such as caustic soda (NaOH), which is useful in the manufacture of pulp and paper, textiles, soaps and detergents.

SUMMARY

[0006] A general schematic illustration of an MEC is shown in FIG. **1**. The MEC **100** includes an anode chamber **112** and a cathode chamber **114** that are separated by a membrane **106**. An anode **102** is disposed in the anode chamber **112**. The anode **102** includes anode-respiring bacteria **108** disposed on the surface of the anode **102**. A cathode **104** is disposed in the cathode chamber **114**. In operation, organics dissolved within an anode solution **118** (e.g., wastewater) are oxidized by the anode-respiring bacteria **108**. The oxidized organics release electrons which are transported to the anode **102**. Concurrently, H_2O in the cathode solution **120** is reduced to H_2 at the cathode **104**, and hydroxyl ions (OH^-) are transported through the membrane **106** to the anode **102**. The reactions may be driven by a power source **110** (e.g., a DC voltage power source) that is operatively connected (e.g., electrically) to the anode **102** and the cathode **104**.

[0007] Practical application of MECs hinges on the ability to achieve high current densities within the MEC at low applied voltages, so that high rates of wastewater treatment and H_2 production can be obtained with reduced MEC energy input. Theoretically, a potential of about 0.14 V must be applied to the MEC to produce H_2; however, practical applied voltages in laboratory systems are greater, since losses of potential occur in MECs due to activation losses at both the anode and the cathode, and Ohmic losses occur that depend upon the nature of the electrolyte used to separate the electrodes, as well as on the separation distance between the electrodes.

[0008] ARB produce maximum current densities in the range of 10 A/m^2 (amps per square meter of the anode), with anode-potential losses of 0.1 to 0.2 V. This loss of potential is the energy that ARB derive for their growth, and thus is unavoidable. For the cathodic H_2-evolution reaction, various metal catalysts can be used to decrease losses of potential, and the activation loss for the reaction depends on the nature of the metal catalyst.

[0009] The conductivity of the anode and cathode solutions and the nature of the membrane used to separate the two electrodes govern the Ohmic losses, which scale linearly with the separation distance between the anode and the cathode. Wastewaters a re typically of poor ionic conductivity; thus, it is important to place the anode and the cathode very close to each other to minimize Ohmic losses. Anion exchange membranes (AEM) may be a better alternative to cation exchange membranes (OEM) for separating the anode and the cathode, because of their low resistance, e.g., to ion transport. In principle, the membrane could be entirely excluded, but removing the membrane requires increasing the distance between the anode and the cathode to avoid H_2 short-circuiting, thus increasing Ohmic losses.

[0010] Thus, in one embodiment, a microbial electrolysis cell is provided. The microbial electrolysis cell includes a high surface-area brush anode, a cathode, a power source operatively connected to the brush anode and the cathode, an anion exchange membrane separating the brush anode from the cathode and a reaction chamber containing the brush anode, the cathode and the anion exchange membrane. The anion exchange membrane operatively separates the reaction chamber into an anode chamber containing the brush anode and a cathode chamber containing the cathode. The brush anode and the cathode are separated by a separation distance that is not greater than about 1.5 cm.

[0011] According to one configuration, the brush anode comprises a plurality of brush fibers emanating from a conductive wire disposed approximately through the center of the anode, where the brush fibers comprise carbon fibers and the conductive wire comprises stainless steel. In another configuration, the cathode comprises a metal foam. For example, the metal foam may be characterized as having a thickness of not greater than about 5 mm. The cathode may also be characterized as comprising nickel metal foam.

[0012] In another configuration, the separation distance between the brush anode and the cathode is not greater than about 1.25 cm. In another characterization, the brush anode has a thickness of not greater than about 2.0 cm. In yet another characterization, the brush anode has a length, where the

brush anode is in direct physical contact with the anion exchange membrane along at least a portion of its length. In another characterization, the cathode is in direct physical contact with the anion exchange membrane.

[0013] In one configuration, the brush anode, the cathode and the anion exchange membrane comprise substantially cylindrical bodies that are disposed in a substantially concentric relationship in a cylindrical electrolysis cell. In one characterization, the anode is disposed on the outside of the cylindrical electrolysis cell. In another characterization, the anode comprises a brush anode that is wound into a cylindrical body. In another characterization, the anode having a brush comprising a plurality of brush fibers emanating from a conductive wire, wherein the brush anode is spirally wound into a cylindrical body.

[0014] In another embodiment, a multi-module microbial electrolysis cell treatment apparatus is provided. The apparatus includes a treatment tank having an inlet for influent and an outlet for effluent, and a plurality of cylindrical microbial electrolysis cells operatively disposed within the treatment tank. The microbial electrolysis cells comprise a high surface-area brush anode, a cathode, a power source operatively connected to the brush anode and the cathode and an anion exchange membrane separating the brush anode from the cathode. Advantageously, the brush anode, the cathode and the anion exchange membrane comprise substantially cylindrical bodies that are disposed in a substantially concentric relationship to form the cylindrical microbial electrolysis cells, where the anion exchange membrane operatively separates the influent from the effluent in the treatment tank.

[0015] In one characterization of the apparatus, the brush anodes are disposed on the outside of the cylindrical electrolysis cells.

[0016] In yet another embodiment, a method for the production of H_2 from a fluid stream comprising organic matter in a microbial electrolysis cell is provided. The method comprises the steps of providing at least one microbial electrolysis cell, the cell comprising an anode disposed in an anode chamber, a cathode disposed in a cathode chamber, a power source operatively connected to the anode and the cathode, and an anion exchange membrane separating the anode and the cathode. The fluid stream is contacted with anode-respiring bacteria disposed on the anode, and the cathode is contacted with a cathode solution comprising H_2O. A gaseous composition comprising at least 98% H_2 may be removed from the cathode chamber.

[0017] In one characterization, the fluid stream comprises a sodium salt. In another characterization, caustic soda is extracted from the cathode chamber. In another characterization, the method includes periodically sparging the anode chamber with air, and/or periodically sparging the cathode chamber with air. The method may also include the step of injecting a CO_2-containing gas into the cathode chamber to reduce the pH of the cathode solution.

[0018] In another characterization, the at least one microbial electrolysis cell comprises a cylindrical microbial electrolysis cell, wherein the anode, the cathode and the anion exchange membrane comprise substantially cylindrical bodies that are disposed in a substantially concentric relationship to form the cylindrical electrolysis cell, and wherein the anion exchange membranes operatively separate the anode chamber from the cathode chamber. In yet another characterization, the brush anodes are disposed on the outside of the cylindrical electrolysis cell whereby the anion exchange membranes operatively separates a single anode chamber from a plurality of cathode chambers configured within the plurality of cylindrical electrolysis cells.

DESCRIPTION OF THE DRAWINGS

[0019] FIG. **1** illustrates a schematic representation of a microbial electrolysis cell (MEC).

[0020] FIG. **2** illustrates a schematic representation of a MEC.

[0021] FIG. **3** illustrates a schematic view of an anode, a cathode and a membrane separating the anode and cathode.

[0022] FIG. **4** illustrates a schematic view of an anode, a cathode and a membrane separating the anode and cathode.

[0023] FIG. **5** illustrates a side (e.g. front) view of brush anode.

[0024] FIG. **6** illustrates a top view of and a perspective view of a MEC.

[0025] FIG. **7** illustrates the comparative Ohmic losses of several different anion exchange membranes used in a MEC.

[0026] FIG. **8** illustrates a top view of a multi-module MEC tank.

DESCRIPTION

[0027] Disclosed herein are designs for a MEC that may achieve high current densities at relatively low applied voltages. The MEC may produce, at the cathode, a high purity H_2 gas stream (e.g., greater than 98% H_2) that can be directly used in energy-conversion applications or as a chemical precursor. Other useful chemical products may also be produced, such as caustic soda (NaOH).

[0028] Microbial electrolysis cell (MEC), as used herein, utilizes electrons produced at the anode for the purpose of generating chemical products at the cathode and not as a significant power source external to the MEC, such as is the case with a microbial fuel cell.

[0029] FIG. **2** illustrates a schematic representation of a MEC. The MEC includes a reaction chamber **226** that is operatively separated into an anode chamber **212** and a cathode chamber **214** by a membrane **206**. The anode chamber **212** includes an anode **202** (e.g., a brush anode) disposed therein and the cathode chamber **214** includes a cathode **204** disposed therein. The anode chamber **212** and cathode chamber **214**, and hence the anode **202** and the cathode **204**, are separated by a membrane **206** (e.g., an anion exchange membrane). In particular, the membrane **206** may be of such a nature and may be configured within the reaction chamber **226** such that reaction products from chambers **212** and **214** cannot intermix.

[0030] The anode **202** may include anode-respiring bacteria **208** (e.g., *G. sulfurreducens*) disposed thereon. The anode **202** may be a three-dimensional, high surface area anode and in one embodiment is a brush anode. For example, the anode **202** may be a carbon brush anode. The anode **202** may also include a conductive wire **216** (e.g., a titanium or stainless steel conductor wire) to facilitate connection of the anode **202** to the power source **210** for the transport of electrons.

[0031] The cathode **204** may be a mesh cathode (e.g., a stainless steel mesh cathode) or the cathode **204** may comprise a metal foam (e.g., a nickel metal foam). The cathode may advantageously be very thin, such as having a thickness of not greater than about 5 mm, such as not greater than about 2 mm, and even not greater than about 1 mm.

[0032] As illustrated in FIG. **2**, the electrolysis cell **200** comprises an anode **202**, a cathode **204**, and a membrane **206** that comprise substantially planar bodies that are disposed in a substantially co-planar relationship. During operation of the cell, an anode solution **218** may be disposed within the anode chamber **212** and a cathode solution **220** may be disposed within the cathode chamber **214**. For example, the anode solution **218** may include organic matter (e.g., dissolved organic matter), such as a waste water stream (e.g., a standard domestic waste water). In this regard, the organics may be oxidized at the anode **202** by the anode-respiring bacteria **208**, and an oxidized carbon gas species (e.g., CO_2) may be removed from the anode chamber **212** at an anode chamber outlet **222**. Concurrently, a cathode solution **220** may be disposed within the cathode chamber **214**, where the cathode solution is comprised mainly of H_2O. Thus, the H_2O may be reduced at the cathode **204** and a gaseous composition comprising H_2 may be withdrawn from the cathode liquid chamber **214** at the cathode chamber outlet **224**.

[0033] FIGS. **3** and **4** illustrate schematic side views of a brush anode separated from a cathode by a membrane. Referring to FIG. **3**, the brush anode **302** comprises a plurality of carbon brush fibers **317** emanating from a conductive wire **316** disposed approximately through the center of the anode **302** and substantially parallel to the surfaces of a membrane **306** and a cathode **304**. The brush anode may advantageously have a length (L) of at least about 5 cm such as at least about 10 cm.

[0034] Referring now to FIG. **4**, a portion of a brush anode **402**, a membrane **406**, and a cathode **404** are illustrated. The brush anode includes carbon brush fibers **417** and anode-respiring bacteria **408** disposed on the carbon brush fibers **417** throughout the thickness (T) of the brush anode **402**. The thickness of the brush anode (e.g., the diameter) may be relatively small, to reduce Ohmic losses in the MEC. For example, the brush anode **402** may have a thickness of not greater than about 2.0 cm, such as not greater than about 1.5 cm, such as not greater than about 1.0 cm and even not greater than about 0.75 cm.

[0035] Further, the separation distance (G) between the tips of the carbon brush fibers **417** (e.g., the tips adjacent the membrane **406**) and the surface of the cathode **404** (e.g., the surface adjacent to the membrane **406**) may be significantly reduced. In one characterization, the separation distance (G) is not greater than about 1.25 cm, such as not greater than about 1.0 cm, not greater than about 0.9 cm, not greater than about 0.8 cm, not greater than about 0.7 cm, not greater than about 0.6 cm, not greater than about 0.5 cm, not greater than about 0.4 cm, and even not greater than about 0.3 cm. In a further characterization, the anode **402**, the cathode **404**, or both may be in physical contact with the membrane **406** along at least a portion of the length thereof. In this manner, the thickness of the membrane **406** will be the separation distance (G) between the anode and cathode. In one aspect, the thickness of the membrane is not greater than about 5 mm, such as not greater than about 1 mm.

[0036] FIGS. **5** and **6** illustrate various facets of a MEC design according to another embodiment. The MEC illustrated in FIGS. **5** and **6** may advantageously reduce Ohmic losses, may produce high purity H_2 (e.g., >99% pure H_2), and/or may have high volumetric current densities and H_2 production rates. This MEC advantageously utilizes cylindrical bodies (e.g., cylindrical bodies of the anode, cathode and membrane) that are disposed in substantially concentric relationship to form a cylindrical electrolysis cell and increase the efficiencies of the MEC.

[0037] In the MEC **600** illustrated in FIG. **6**, the brush anode **602** may be wound around (e.g., onto) the cylindrical assembly of a membrane **606** and a cathode **602** along its length. The length of the cylindrical assembly **600** may be selected as per the requirements for treatment and H_2-production performance.

[0038] The AEM **606** is rolled over a cylindrical stainless steel mesh that acts as the cathode **604**. A 316-grade stainless steel mesh may be used for the cathode **604** in the present MEC design, but any grade stainless steel may be used as long as it has appreciable nickel content. Carbon cloths coated with nickel or other metal catalyst powders can also be used in the MEC **600**.

[0039] Other materials that are comparable in cost to stainless steel, may be used for the cathode **604**. For example, a nickel mesh or a metal foam (e.g., a nickel metal foam) may be used in the form of hollow cylinders. This nickel mesh or metal foam should be relatively thin to minimize Ohmic losses, and may advantageously have a thickness of not greater than about 5 mm, such as not greater than about 2 mm, or even not greater than about 1 mm.

[0040] As is discussed with respect to FIGS. **3** and **4**, the MEC **600** may utilize a relatively short separation distance between the anode **602** and the cathode **604** to reduce Ohmic losses. As used herein, the separation distance is measured from outer surface to outer surface, e.g., from the tips of the anode brush to the surface of the cathode mesh. See FIG. **4**. The separation distance may be not greater than about 1.5 cm, such as not greater than about 1.25 cm, or even not greater than about 1.0 cm. In one characterization, the separation distance is approximately 0.5 cm. For a 100-mM PBS (phosphate buffer solution), which has conductivity of 14 mS/cm, a distance of 3 results in an Ohmic loss of 0.42 V at 20 A/m , while the Ohmic loss in the disclosed

[0041] MEC configuration having 0.5 cm separation distance may be reduced to as low as 0.07 V.

[0042] As discussed above, an AEM may advantageously be used in the MEC design to separate the anode and the cathode. When a membrane (e.g., an AEM) is used to separate the anode and the cathode, a pH gradient develops and results in additional losses of potential. While a pH gradient exists when using an AEM, the cathode pH is lower and additional methods to mitigate the cathode pH (e.g., CO_2 addition to the cathode) may also be utilized.

[0043] An AEM sold under the trade name AMI-7001 (Membranes International, Ringwood N.J., USA) is believed to be the most widely used AEM in MECs. AMI-7001 is a strong base anion exchange membrane utilizing quaternary ammonium as a functional group. However, is has been discovered that this membrane introduces too much loss in an MEC due to its resistance to ion flow. Five AEMs are evaluated for the present MEC design. The resistance that each provides to ion flow in 100-mM phosphate buffer solution (PBS) is illustrated in FIG. **7**. As it gives the best performance, the A201 membrane (Tokuyama Corp., Tokyo, JP) may advantageously be utilized in the disclosed MEC design. This membrane is a hydrocarbon polymer membrane containing quaternary ammonium moieties.

[0044] The MECs disclosed herein may provide high operating efficiencies when used to treat fluid streams containing organic matter (e.g., wastewater fluid streams) and produce a

gas composition comprising H_2 gas. More specifically, relatively low applied voltages may be utilized to provide relatively high current densities in the cell. In one aspect, the applied voltage (i.e., across the anode and the cathode) is not greater than about 1.2 V, and the resulting volumetric current density is at least about 500 A/m^3, such as at least about 600 A/m^3 or even at least about 750 A/m^3.

[0045] The present MEC designs may provide other important advantages. One is the ability to collect pure H_2 at the cathode. In one aspect, the gas composition withdrawn from the cathode chamber comprises at least 95% H_2, such as at least 98% H_2, at least 98.5% H_2, at least 99% H_2, at least 99.5% H_2 or even at least 99.9% H_2. A second advantage is that the membrane creates a significant resistance to diffusion of H_2 across to the anode, and this reduces H_2 loss to biological activity at the anode. Scaled-up MECs not containing a membrane have shown poor H_2 recovery caused by extensive CH_4 formation as a result of H_2 consumption by methanogens. The MEC designs disclosed herein may substantially preclude this problem. In one aspect, the gas composition withdrawn from the cathode chamber comprises substantially no CH_4 (e.g., not greater than 0.1% CH_4). Methane production, however, may still occur at the anode, from acetate (Ac^-) and H_2 produced from fermentation reactions, and this diverts electrons away from electrical current, and ultimately decreases H_2 production. Thus, periodical sparging of the anode chamber with air or other O_2-containing gas may be implemented, for operation at large scale. This curbs the growth of methanogens, as they are severely inhibited by O_2, while dominant ARB such as those belonging to the *Geobacter* genus are reported to tolerate O_2 to certain extent. In the unlikely event of methanogenesis at the cathode, a similar strategy could also be applied to the cathode to limit methane formation.

[0046] While a single MEC module is described above, a multi-module apparatus may be assembled to achieve wastewater treatment at flows typically generated by industries or municipalities. Scaling may be achieved by using multiple modules. FIG. **8** illustrates a design of a multi-module MEC treatment tank **850** that is capable of a high volumetric treatment rate. The tank **850** may consist of several modules **800** of the anode, membrane and cathode configuration described above (e.g., FIG. **6**). The height and diameter of the individual modules **800**, and the distance between any two modules can be selected as per the requirement for treatment performance, as long as within a single module **800** the effective distances between the anode and the cathode are maintained as is disclosed above.

[0047] In addition to high purity hydrogen, caustic soda (NaOH) may be produced in the current MEC designs. The present MEC designs will allow the production of caustic soda at high rates, but with lower applied voltages. Caustic soda is produced in MECs via the formation of OH^- at the cathode from the water reduction reaction, and the transfer of Na^+ from the anode to the cathode through a cation exchange membrane. Although an AEM is typically used in the MECs disclosed herein, caustic soda can still be produced if NaCl is added to the cathode solution. In this case, the Cl^- ions move from the cathode to the anode, leaving behind Na^+ that combine with OH^-. The MECs disclosed herein reduces Ohmic losses, thus allowing for faster ion movement and thus higher rates of caustic production at a given applied voltage.

[0048] In summary, the MECs disclosed herein and the methods disclosed herein advantageously enable a scalable technology that may be optimized for the low-energy treatment of organic materials such as in wastewaters. The wastewaters may be domestic wastewaters or may be industrial wastewaters such as those that are common to the food and beverage processing industries. For example, the wastewater may be an industrial wastewater from a potato treatment plant (e.g., in the manufacture of potato snacks), breweries, wineries, confectioneries, dairies, fruit processing plants, frozen dinner product plants, soy product plants, grain processing plants and pulp and paper manufacturing plants. The methods may use about 70% less electricity and produce about 80% less solid sludge as compared to aeration methods for the treatment of wastewater, while delivering identical or improved treatment performance. Hydrogen generated by the method may be used as a versatile commodity chemical or as a carbon-free energy source. Caustic soda as a byproduct may also be used in many food and beverage production plants. The MEC is advantageously low-maintenance, energy efficient and may be assembled without the use of exotic materials. The MECs may advantageously provide a high-surface area for bacterial growth, translating into efficient contaminant breakdown in the wastewater stream. The MECs are easily scaled to treat high volumes of wastewater.

[0049] While various embodiments of the present invention have been described in detail, it is apparent that modifications and adaptations of those embodiments will occur to those skilled in the art. However, is to be expressly understood that such modifications and adaptations are within the spirit and scope of the present invention.

What is claimed is:

1. A microbial electrolysis cell, comprising:

a high surface-area brush anode;

a cathode;

a power source operatively connected to the brush anode and the cathode;

an anion exchange membrane separating the brush anode from the cathode; and

a reaction chamber containing the brush anode, the cathode and the anion exchange membrane

wherein a separation distance between the brush anode and the cathode is not greater than about 1.5 cm, and wherein the anion exchange membrane operatively separates the reaction chamber into an anode chamber containing the brush anode and a cathode chamber containing the cathode.

2. The microbial electrolysis cell of claim **1**, wherein the brush anode comprises a plurality of brush fibers emanating from a conductive wire disposed approximately through the center of the anode, wherein the brush fibers comprise carbon fibers and the conductive wire comprises stainless steel.

3. The microbial electrolysis cell of claim **1**, wherein the cathode comprises a metal foam.

4. The microbial electrolysis cell of claim **3**, wherein the metal foam has a thickness not greater than about 5 mm.

5. The microbial electrolysis cell of claim **1**, wherein the cathode comprises nickel metal foam.

6. The microbial electrolysis cell of claim **1**, wherein the separation distance between the brush anode and the cathode is not greater than about 1.25 cm.

7. The microbial electrolysis cell of claim **1**, wherein the brush anode has a thickness of not greater than about 2.0 cm.

8. The microbial electrolysis cell of claim **1**, wherein the brush anode has a length, wherein the brush anode is in direct physical contact with the anion exchange membrane along at least a portion of its length.

9. The microbial electrolysis cell of claim **1**, wherein the cathode is in direct physical contact with the anion exchange membrane.

10. The microbial electrolysis cell of claim **1**, wherein the brush anode, the cathode and the anion exchange membrane comprise substantially cylindrical bodies that are disposed in a substantially concentric relationship in a cylindrical electrolysis cell.

11. The microbial electrolysis cell of claim **10**, wherein the anode is disposed on the outside of the cylindrical electrolysis cell.

12. The microbial electrolysis cell of claim **10**, wherein the anode comprises a brush anode that is wound into a cylindrical body.

13. The microbial electrolysis cell of claim **10**, wherein the anode comprises a brush comprising a plurality of brush fibers emanating from a conductive wire, wherein the brush anode is spirally wound into a cylindrical body.

14. A multi-module microbial electrolysis cell treatment apparatus, comprising:

a treatment tank having an inlet for influent and an outlet for effluent; and

a plurality of cylindrical microbial electrolysis cells operatively disposed within the treatment tank, the microbial electrolysis cells comprising:

a high surface-area brush anode;

a cathode;

a power source operatively connected to the brush anode and the cathode; and

an anion exchange membrane separating the brush anode from the cathode,

wherein the brush anode, the cathode and the anion exchange membrane comprise substantially cylindrical bodies that are disposed in a substantially concentric relationship to form the cylindrical microbial electrolysis cells, and wherein the anion exchange membrane operatively separates the influent from the effluent in the treatment tank.

15. The multi-module microbial electrolysis cell treatment apparatus of claim **14**, wherein the brush anodes are disposed on the outside of the cylindrical electrolysis cells.

16. A method for the production of H_2 from a fluid stream comprising organic matter in a microbial electrolysis cell, comprising the steps of:

providing at least one microbial electrolysis cell comprising:

an anode disposed in an anode chamber,

a cathode disposed in a cathode chamber,

a power source operatively connected to the anode and the cathode, and

an anion exchange membrane separating the anode and the cathode,

contacting the fluid stream with anode-respiring bacteria disposed on the anode;

contacting the cathode with a cathode solution comprising H_2O; and

removing, from the cathode chamber, a gaseous composition comprising at least 98% H_2.

17. The method of claim **16**, wherein the fluid stream comprises a sodium salt.

18. The method of claim **16**, further comprising the step of extracting caustic soda from the cathode chamber.

19. The method of claim **16**, further comprising the step of periodically sparging the anode chamber with air.

20. The method of claim **16**, further comprising the step of periodically sparging the cathode chamber with air.

21. The method of claim **16**, comprising the step of injecting a CO_2-containing gas into the cathode chamber to reduce the pH of the cathode solution.

22. The method of claim **16**, wherein the at least one microbial electrolysis cell comprises at least one cylindrical microbial electrolysis cell, wherein the anode, the cathode and the anion exchange membrane comprise substantially cylindrical bodies that are disposed in a substantially concentric relationship to form the cylindrical electrolysis cells, and wherein the anion exchange membranes operatively separate the anode chamber from the cathode chamber.

23. The method of claim **22**, wherein the brush anodes are disposed on the outside of the cylindrical electrolysis cell whereby the anion exchange membranes operatively separates a single anode chamber from a plurality of cathode chambers configured within the plurality of cylindrical electrolysis cells.

* * * * *

US 20100190039A1

(19) **United States**

(12) **Patent Application Publication**

Hamelers et al.

(10) **Pub. No.: US 2010/0190039 A1**

(43) **Pub. Date: Jul. 29, 2010**

(54) **DEVICE AND METHOD FOR CONVERTING LIGHT ENERGY INTO ELECTRICAL ENERGY**

(75) Inventors: **Hubertus Victor Marie Hamelers**, Heelsum (NL); **David Petrus Bonifacius Theodorus Bernardus Strik**, Wageningen (NL); **Jan Frederik Hendrik Snel**, Wageningen (NL); **Cees Jan Nico Buisman**, Harich (NL)

Correspondence Address:
FOLEY AND LARDNER LLP
SUITE 500
3000 K STREET NW
WASHINGTON, DC 20007 (US)

(73) Assignee: **Plant-e-Knowledge B.V.**

(21) Appl. No.: **12/596,298**

(22) PCT Filed: **Apr. 17, 2008**

(86) PCT No.: **PCT/NL2008/050219**

§ 371 (c)(1),
(2), (4) Date: **Apr. 7, 2010**

(30) **Foreign Application Priority Data**

Apr. 17, 2007 (NL) 2000598

Publication Classification

(51) **Int. Cl.**
H01M 8/16 (2006.01)

(52) **U.S. Cl.** **429/2**

(57) **ABSTRACT**

The invention relates to a device comprising a reactor, where the reactor comprises an anode compartment and a cathode compartment, and where the anode compartment comprises a) an anodophilic micro-organism capable of oxidizing an electron donor compound, and b) a living plant or part thereof. The invention also relates to a method for converting light energy into electrical energy and/or hydrogen, where a feedstock comprising an electron donor compound is introduced into the device.

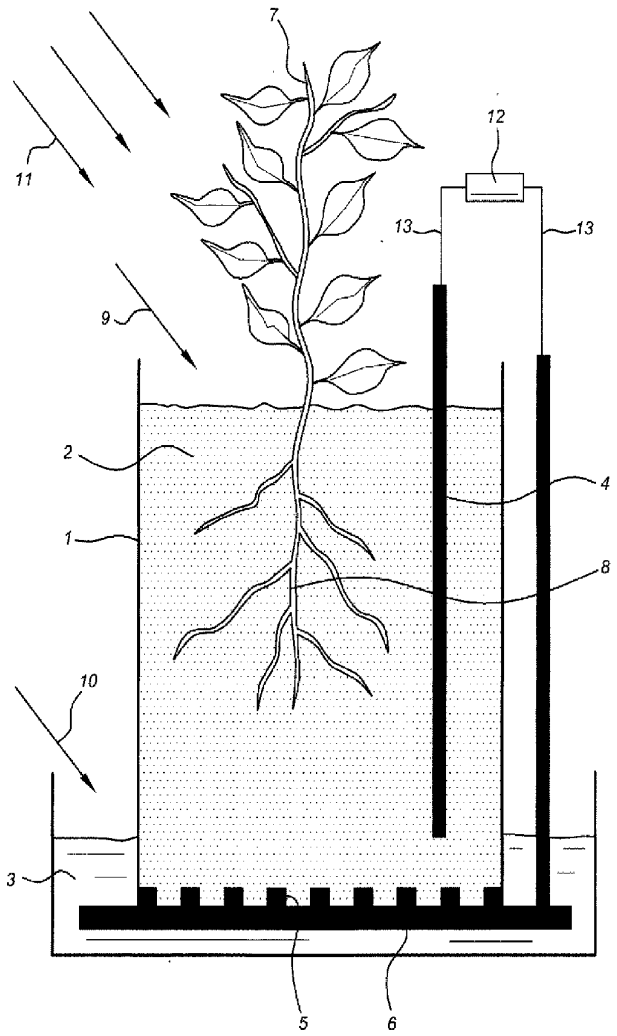


Fig 1

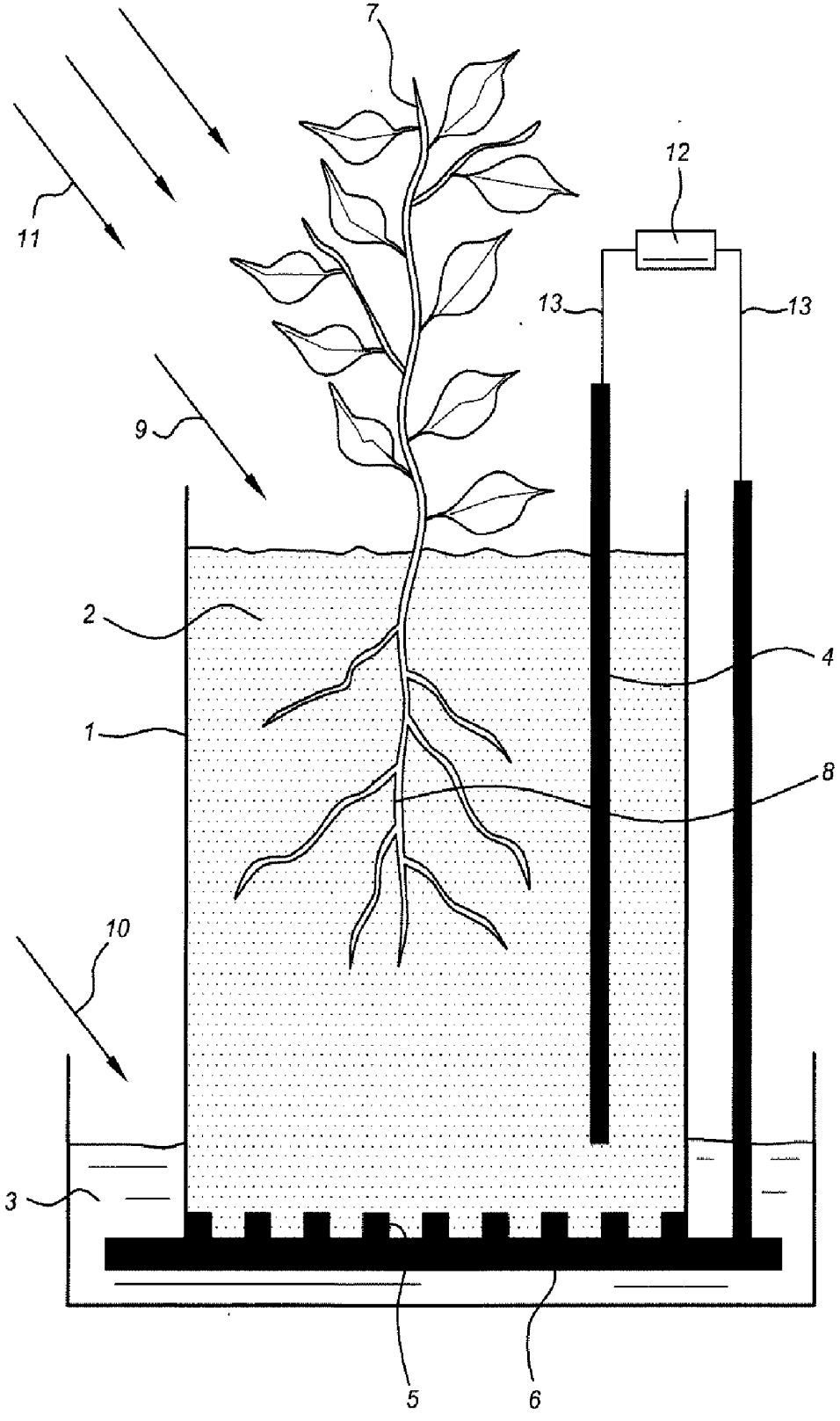
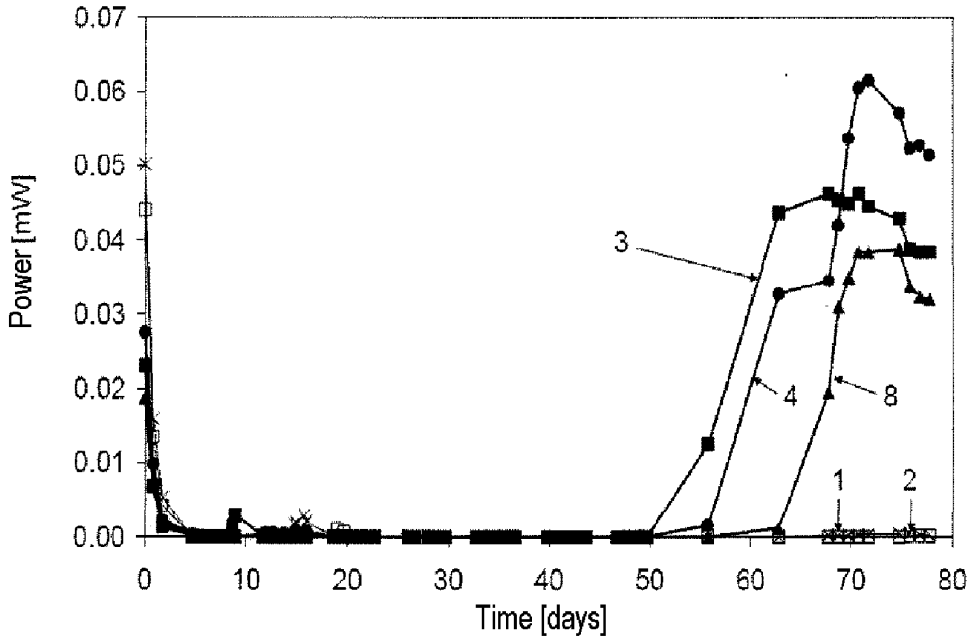


Fig 2


0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Power [mW]
0
10
20
30
40
50
60
70
80
Time [days]
3
4
8
1
2

DEVICE AND METHOD FOR CONVERTING LIGHT ENERGY INTO ELECTRICAL ENERGY

FIELD OF THE INVENTION

[0001] The present invention relates to a device and a method for converting light energy into electrical energy and/or hydrogen by using a living plant for converting light energy into a feedstock for a microbial fuel cell.

BACKGROUND TO THE INVENTION

[0002] Microbial fuel cells are known from the prior art. For example, WO 2007/006107 discloses a microbial fuel cell that comprises a reactor, and each reactor comprises an anode compartment, a cathode compartment and a membrane, where the membrane separates the anode compartment and the cathode compartment from each other. The anode compartment contains micro-organisms capable of oxidizing organic electron donor compounds, the electrons being supplied to the anode in the anode compartment. According to WO 2007/006107, the organic electron donor compound in question can be glucose, sucrose, an acetate or a reducing compound of the type occurring for example in domestic sewage and the effluent of bio-refineries.

[0003] Other microbial fuel cells are described for example in: Logan et al., 2006, Lovley, 2006a; Lovley, 2006b; Rabaey and Verstraete, 2005, and Verstraete and Rabaey, 2006. The oxidation of the electron donor compounds can be catalysed for example by anodophilic and/or cathodophilic micro-organisms and redox enzymes. In some applications, hydrogen is produced in the cathode compartment as an energy carrier, instead of electricity (Liu et al., 2005; Rozendal et al., 2006).

[0004] Some fuel cells are designed in such a way that it is possible to transform photosynthetic activities into electricity. U.S. Pat. No. 3,477,879 discloses a device for converting light energy into electrical energy, where the device consists of an anode compartment containing an aqueous medium, where this aqueous medium contains live and dead algae and minerals, including sulphide, that occur in sea water, and a cathode compartment containing an aqueous medium, where this aqueous medium contains bacteria and minerals, including sulphate, that occur in sea water. The anode compartment and the cathode compartment are connected by an ion bridge or "salt bridge". The live algae are capable of producing oxygen. When the device is in operation, dead algae are pumped from the anode compartment into the cathode compartment, where they serve as a nutrient for the bacteria that are capable of converting sulphate into sulphide. When sulphate is converted into sulphide, electrons are taken up. Sulphide is converted into sulphate and hydrogen ions (H^+) at the cathode, as a result of which electrons are released at the cathode which are taken up again by oxygen via the anode, and the oxygen is then converted into hydroxide ions (OH^-). The hydrogen ions and the hydroxide ions diffuse across the salt bridge and combine to form water, which completes the electrical circuit.

[0005] U.S. Pat. No. 4,117,202 and CA 1,099,332 disclose a biological electrical cell, where use is made of isolated mesophilic cells derived from what are called C_4 plants, i.e. plants capable of converting CO_2 into organic compounds containing four carbon atoms, for example oxalacetate, aspartate and malate. Such cells are also described in Rosenbaum et al., 2005a and Rosenbaum et al., 2005b. Isolated C_4 photosynthesizing plant cells, green algae or (hydrogen producing) bacteria are used in these devices.

[0006] A disadvantage of the microbial fuel cells according to WO 2007/006107 is that an effluent stream such as domestic waste water is used. Effluent streams are not sustainable or renewable, and cannot be sustainably obtained, due to transport, for example. A great deal of energy is invested before effluent streams are obtained, and this involves a large CO_2 emission from fuels, for example fossil fuels or radioactive waste released in the generation of nuclear energy. It is true that by increasing the production of effluent streams, more energy can be produced by fuel cells, but such a method does not offer a sustainable or renewable solution for the increasing world consumption of electrical energy. It is therefore better to generate or regenerate energy in a sustainable or renewable way. The present invention provides a solution for the problem of reducing non-sustainable and non-renewable energy.

SUMMARY OF THE INVENTION

[0007] The present invention relates to a device that comprises a reactor, where the reactor comprises an anode compartment and a cathode compartment and where the anode compartment comprises a) an anodophilic micro-organism capable of oxidizing an electron donor compound, and b) a living plant or part thereof.

[0008] The present invention also relates to a method for converting light energy into electrical energy and/or hydrogen, where a feedstock comprising an electron donor compound is introduced into a device that comprises a reactor, where the reactor comprises an anode compartment and a cathode compartment and where the anode compartment comprises a) an anodophilic micro-organism capable of oxidizing an electron donor compound, and b) a living plant or part thereof.

DETAILED DESCRIPTION OF THE INVENTION

[0009] The verb "to comprise" as is used in this description and in the claims and its conjugations are used in its non-limiting sense to mean that items following the word are included, but items not specifically mentioned are not excluded. In addition, reference to an element by the indefinite article "a" or "an" does not exclude the possibility that more than one of the element are present, unless the context clearly requires that there is one and only one of the elements. The indefinite article "a" or "an" thus usually means "at least one".

[0010] The term "living plant or part thereof" is used in this document in the sense of a plant (or any part thereof) belonging to the Plant Kingdom (Plantae) and comprising at least one eucaryotic cell with a cell membrane, capable of converting light energy into an electron donor compound by means of photosynthesis. The term "living plant or part thereof" therefore also covers separate, possibly undifferentiated plant cells that are obtained for example by tissue culture and are capable of converting light energy, by means of photosynthesis, into an electron donor compound, plants or their parts which are (partly) dead, and algae.

[0011] According to the invention, the electron donor compound is converted into electrical energy and/or chemical energy, preferably in the form of hydrogen, with the aid of an anodophilic micro-organism.

[0012] According to the invention, the electron donor compound is preferably an organic compound.

[0013] A membrane that can transport ions selectively can be used to separate the anode compartment from the cathode compartment. It is also possible to employ electrically non-conducting, non-ion-selective porous materials. Examples of these materials are glass and plastic. However, a membrane that can transport ions selectively is preferred. The membrane is preferably a cation-selective membrane and more preferably a proton-selective membrane.

[0014] The plant or its part is preferably derived from what is called an energy plant. An energy plant is a living plant that contributes to sustainable energy: solar energy is present during the daytime and can be stored by living plants or their parts for example in the form of an electron donor compound, while CO_2 is absorbed from the atmosphere. Hence, an energy plant is to be understood as a living plant capable of converting light energy into chemical energy.

[0015] Various parts of a plant, for example fallen leaves or roots that have not been harvested, can be used as an energy plant. These parts are lost from renewable energy supply. A large part of the solar energy stored by the plant leaves the plant under the ground, due to the roots dying and respiring and by the release of an exudate. This process stimulates the growth of soil micro-organisms. These processes are defined as rhizodeposition. It has been established that nearly all types of chemical components of a plant can be lost by root losses. These components are for example carbohydrates such as sugars, amino acids, organic acids, hormones and vitamins. These components are classified into 4 groups, depending on their origin: exudates, secretions, lysates and gases. Exudates seep out of the root without the involvement of metabolic energy, while in the case of secretions, proper metabolic processes take place in the plant. Lysates are due to the root dying off. Gases also come from the roots of the plant (Lynch, 1990). Rhizodeposition depends for example on the type of the plant, its age and circumstances of life. Cast-off plant parts such as fruits, branches and leaves can contribute to the increase of organic matter in the soil. It is therefore preferred according to the invention that the plant or part thereof is an energy plant or a part thereof, in which case the living plant or part thereof converts light energy into at least an electron donor compound, which is subsequently converted into electrical energy and/or hydrogen, preferably by the root system of a living plant, in cooperation with a micro-organism.

[0016] According to the invention, the electron donor compound can be present in exudates, secretions, lysates, vegetable matter from dead plant parts, gases and/or a gum of plant origin, derived from the root system of a plant or a part thereof. The electrons produced by micro-organisms are transported from the anode first to a resistance or a device that consumes electrical energy, and then to the cathode. Oxygen, especially oxygen from the atmosphere, is used as the terminal electron acceptor.

[0017] According to an embodiment of the present invention, the anode preferably comprises an anodic material, said anodic material preferably being selected from the group consisting of graphite granules, graphite felt, graphite rods, other graphite-containing electron conductors and combinations of one or more of such materials, the root zone of a living plant essentially being present in the anodic material. This means in particular that the roots of the living plant are mainly placed in the anodic material. The added advantage of this is that the plant has a grip.

[0018] The micro-organism that converts the electron donor compound of the plant or part thereof preferably lives around the root zone of the living plant (called the rhizosphere), so the micro-organism can release electrons to the anode more easily.

[0019] In another embodiment according to the present invention, the reactor comprises a number of anode compartments, which are closed off from the surroundings (the atmosphere).

[0020] In yet another embodiment according to the present invention, the reactor comprises an anode compartment that can be opened, so that it can be in contact with the surroundings thereof. This has the advantage that the living conditions of the living plant, such as temperature, light and/or moisture, can be regulated.

[0021] According to the invention, the feedstock for the anode compartment can be one or more micro- and/or macronutrients and/or water for the living plant or part thereof or for the micro-organism. The feedstock is preferably a balanced amount of micro- and/or macronutrients and water.

[0022] According to the invention, it is preferable for the anode compartment to comprise a redox mediator (also called an electron shuttle), so that the electron transport in the anode compartment is made easier.

[0023] In another preferred embodiment, the device comprises a number of components that reduce or prevent the production of methane in the anode compartment.

[0024] Living plants evaporate water that has been taken up for example by the root system. Therefore, an embodiment of the device according to the invention is equipped with an overflow for the removal of excess feedstock introduced into the anode compartment. In another preferred embodiment, this overflow leads from the anode compartment to the cathode compartment.

[0025] The invention is explained in more detail with the aid of FIG. **1**. FIG. **1** shows a reactor **1** that is provided with an anode compartment **2** and a cathode compartment **3**. The anode compartment **2** contains an anode **4**, and the cathode compartment **3** contains a cathode **5**. The anode compartment **2** and the cathode compartment **3** are separated from each other by a membrane **6**. The anode compartment **2** accommodates a living plant **7**, placed in it in such a way that the roots **8** of the living plant are surrounded by the anodic material in granular form. Both the anode compartment and the cathode compartment are in contact with the surroundings—see the arrows **9** and **10**. Light energy **11**, for example sunlight, can reach the living plant directly. Oxygen (coming from the atmosphere) can diffuse into the cathode compartment. The anode and the cathode are connected electrically with each other by a resistance or a device that consumes electrical energy (**12**), with the aid of electrical connections **13**.

EXAMPLE

[0026] Eight vertically placed tubular microbial fuel cells were made from Schott Duran glass. The height of each tube was 30 cm and its diameter was 3.5 cm. At a height of 2 cm and 28 cm, there was a glass side-arm, the lower of which was closed off with a rubber bung and the upper kept open to ensure an overflow function. The top end of the tube was left open, so that the above-ground part of the plant protruded

there. A cation exchange membrane (FKL type, FuMA-tech GmbH, St. Ingbert, Germany) was placed at the bottom with the aid of a GL45 screw cap that had a cut-out in it (diameter: 3 cm). A 3-mm-thick graphite felt (FMI Composites Ltd., Galashiels, Scotland) was placed on the inside of the glass tube. A graphite rod (measurements: 26×14×6 mm; Müller & Rössner GmbH & Co., Sieburg, Germany) was introduced into the graphite felt. The tube was then filled with graphite granules (diameter between 1.5 and 5 mm; Le Carbone, Belgium). A 3-mm-thick graphite felt (measurements: 8×8 cm; FMI Composites Ltd., Galashiels, Scotland) was then placed at the bottom of a large glass beaker. On this graphite felt were then placed the glass tube and, parallel to it, a second graphite rod. The anodic electrode and the cathodic electrode were formed by the graphite components inside and outside the glass tube, respectively. The (electrical) circuit of the anode and cathode was completed by plastic-coated copper wires running from the graphite rods to the external resistance R of 1000 Ohms.

[0027] The electrode potentials and the cell voltage [E (cell) in mV] were measured off-line with a Multimeter (True RMS Multimeter, Fluke 189). Ag/AgCl reference electrodes (ProSense Qis, Oosterhout, Netherlands) were used for measuring the electrode potentials. The cell voltage was determined continuously with the aid of FieldPoint FP-AI-110 modules (National Instruments, Netherlands), a personal computer (Pentium III) and a self-programmed Labview 7.0 program (National Instruments, Netherlands). The current intensity (I in mA) was then calculated from Ohm's law [I=E (cell)/R]. The power output (P in watts) of the microbial fuel cell was calculated from the cell voltage and the current intensity [P=I×E (cell)].

[0028] The light was provided by a 250 W metal halogen lamp (Spacesaver C/TLBH250), later supplemented by a 400 W metal halogen lamp (Spacesaver C/TLBH400), placed at a height of 125 cm above the table that supported the experimental assembly. The room accommodating the microbial fuel cell was lit by TL tubes and indirect sunlight. White screens above and on two sides of the assembly ensured the reflection of light. The lamps were kept on for 14 hours during the day with the aid of a time switch, after which they were switched off for 10 hours at night. The assembly was housed in a room kept at room temperature (about 20-25° C.). From day 26, the temperature was measured on-line with a copper-constantan thermocouple and recorded by a Fieldpoint (FP) module, using the abovementioned personal computer and program. The temperature was in the region of 24-27° C.

[0029] The anode compartments of the microbial fuel cell were primed with a modified Hoagland nutrient solution (Taiz and Zeiger, 2006), with extra micronutrients for e.g. the micro-organism. The solution had the following composition, with the concentrations in mg per liter given in brackets: KNO_3 (606.60), $Ca(NO_3)_2 \cdot 4H_2O$ (944.64), $NH_4H_2PO_4$ (230.16), $MgSO_4 \cdot 7H_2O$ (246.49), KCl (3.73), H_3BO_3 (1.55), $MnSO_4 \cdot H_2O$ (0.34), $ZnSO_4 \cdot 7H_2O$ (0.58), $CuSO_4 \cdot 5H_2O$ (0.12), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.09), H_2MoO_4 with 85% of MoO_3 (161.97), $CoCl_2 \cdot 6H_2O$ (2.00), Na_2SeO_3 (0.10), EDTA as Titriplex II (30.00), $FeCl_2 \cdot 4H_2O$ (10.68), $Ni_2Cl \cdot 6H_2O$ (0.06), $Na_2SiO_3 \cdot 9H_2O$ (284.20).

[0030] The solution was neutralized to a pH of about 7 with 2M NaOH. It was inoculated with the effluent from another operating microbial fuel cell. Potassium acetate (KAc) was introduced as the feedstock in batches, so that the anodophilic micro-organisms, amongst others, would proceed to multiply in the fuel cell. The cathode compartment was filled with 50 mM $K_3Fe(CN)_6$ and 100 mM KH_2PO_4, which were neutralized to a pH of about 7. This solution was later replaced by demineralised water with 2 ml of phosphate buffer per liter (K_2HPO_4 132.7 g/l^{-1}; KH_2PO_4: 168.5 g/l^{-1}). The volume of the anode liquid and the volume of the cathode liquid amounted to about 250 and 200 ml, respectively.

[0031] The acetate was consumed in the microbial fuel cells, and the cell voltage over the anode and cathode was measured. When this cell voltage had dropped, all the graphite granules were removed from the assembly and saved. The residual KAc was removed as far as possible by rinsing the graphite granules with the nutrient medium. Extra graphite granules were then introduced, and the KAc concentration was determined. After this, the granules were distributed over the eight microbial fuel cells.

[0032] A collection of reed sweet grass (*Glyceria maxima,* synon. *Glyceria aquatica*) was obtained from the bed of a brook at Renkum (the Netherlands). The stems of the reed sweet grass were separated (which sometimes called for cutting through the horizontal rhizome) and thoroughly washed, so that the organic matter was removed. The brown parts of the plant were cut off, so that only green plants of reed sweet grass remained. Wet reed sweet grass plants were placed in the anode compartment of six microbial fuel cells (numbers 3 to 8), using 20 to 30 plants per cell. Two microbial fuel cells did not receive any living plants but were treated in the same way as the other microbial fuel cells and acted as reference samples (microbial fuel cells number 1 and 2).

[0033] The level of the anode liquid dropped during the experiment, due to evaporation. It was regularly replenished with demineralised water (up to day 13) or with Hoagland nutrient solution (on days 13-19), or with Hoagland nutrient solution with a buffer (4 ml/l with K_2HPO_4 132.7 g/l; KH_2PO_4: 168.5 g/l) (on days 19 to 34), or with Hoagland solution without any nitrogen, having the following composition, the concentration in mg per liter being given in brackets: $MgSO_4 \cdot 7H_2O$ (246.49), KCl (3.73), H_3BO_3 (1.55), $MnSO_4 \cdot H_2O$ (0.34), $ZnSO_4 \cdot 7H_2O$ (0.58), $CuSO_4 \cdot 5H_2O$ (0.12), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.09), H_2MoO_4 with 85% of MoO_3 (161.97), $CoCl_2 \cdot 6H_2O$ (2.00), Na_2SeO_3 (0.10), EDTA as Titriplex II (30.00), $FeCl_2 \cdot 4H_2O$ (10.68), $Ni_2Cl \cdot 6H_2O$ (0.06), $Na_2SiO_3 \cdot 9H_2O$ (284.20) with a buffer (4 ml/l^{-1} with K_2HPO_4 132.7 g/l^{-1}; KH_2PO_4: 168.5 g/l^{-1}) (from day 34 to the end). A pump, installed on day 23, was used to introduce the nutrient solution at 15-minute intervals, under the control of a time switch. Any excess medium flowed into a receiving flask via an overflow.

[0034] The level of the cathode liquid also dropped during the experiment. It was replenished regularly by the addition of demineralised water. On day 14, the cathode liquid was replaced with a new cathode liquid, which contained demineralised water with a phosphate buffer (K_2HPO_4 132.7 g/l^{-1}; KH_2PO_4: 168.5 g/l^{-1}; 2 ml/l). The graphite cloth in the cathode was replaced here with a new piece of cloth. It was noticed that some previous cathode liquid remained in the cathode compartment, possibly coming from the membrane.

[0035] FIG. **2** shows the power output of three microbial fuel cells with reed sweet grass (numbers **3**, **4** and **8**) and the two reference fuel cells (numbers **1** and **2**) for days 1 to 78. The maximum specific power, measured off-line, was 0.062 mW. The reference assemblies did not produce any electric

energy, but the assemblies with reed sweet grass did. The reed sweet grass plants remained vital and grew during this experiment as well.

REFERENCES

[0036] H. Liu, S. Grot and B. E. Logan (2005): "Electrochemically assisted microbial production of hydrogen from acetate", *Environmental Science and Technology,* 39, No. 11 (2005) pp. 4317-4320

[0037] B. E. Logan, B. Hamelers, R. Rozendal, U. Schroder, J, Keller, S. Freguia, P. Aelterman, W. Verstraete and K. Rabaey (2006): "Microbial fuel cells: Methodology and technology", *Environmental Science and Technology,* 40 (2006) pp. 5181-5192

[0038] B. E. Logan and J. M. Regan (2006): "Electricity-producing bacterial communities in microbial fuel cells", *Trends in Microbiology,* 14, No. 12 pp. 512-518

[0039] D. R. Lovley (2006a): "Bug juice: harvesting electricity with micro-organisms", *Nature Reviews Microbiology,* 4 pp. 497-508

[0040] D. R. Lovley (2006b): "Microbial fuel cells: novel microbial physiologies and engineering approaches", *Current Opinion in Biotechnology,* 17 pp 327-332

[0041] J. M. Lynch: "The Rhizosphere", John Wiley & Sons, 1990

[0042] K. Rabaey and W. Verstraete (2005); "Microbial fuel cells: sustainable core technology", *Trends in Biotechnology,* 23 pp. 291-298

[0043] M. Rosenbaum, U. Schroder and F. Scholz (2005a): "Utilizing the green alga *Chlamydomonas reinhardtii* for microbial electricity generation: A living solar cell", *Applied Microbiology and Biotechnology,* 68 pp. 753-756

[0044] M. Rosenbaum, U. Schroder and F. Scholz (2005b): "In situ electrooxidation of photobiological hydrogen in a photobioelectrochemical fuel cell based on *Rhodobacter sphaeroides", Environmental Science and Technology,* 39 pp. 6328-6333

[0045] R. A. Rozendal, H. V. M. Hamelers, G. J. W. Euverink, S. J. Metz and C. J. N. Buisman (2006): "Principle and perspectives of hydrogen production through biocatalyzed electrolysis", *Int. J. Hydrogen Energy,* 31 pp. 1632-1640

[0046] L. Taiz and E. Zeiger (2006): "Plant Physiology", Sinauer Associates, Inc., Sunderland, USA

1-20. (canceled)

21. A reactor comprising:

(a) an anode compartment comprising an anodic material and (i) an anodophilic micro-organism capable of oxidizing an electron donor compound and (ii) a living plant or part thereof having a root zone, wherein the root zone is placed in the anodic material; and

(b) a cathode compartment.

22. The reactor according to claim **21**, wherein the electron donor compound is an organic compound.

23. The reactor according to claim **21**, wherein the anode compartment and the cathode compartment are separated by a membrane.

24. The reactor according to claim **23**, wherein the membrane is an ion-selective membrane.

25. The reactor according to claim **24**, wherein the membrane is a proton-selective membrane.

26. The reactor according to claim **21**, wherein the plant is a plant capable of converting light energy into chemical energy.

27. The reactor according to claim **21**, wherein the anodic material comprises graphite granules, graphite felt, graphite rods, other graphite-containing electron conductors, or combinations thereof.

28. The reactor according to claim **21**, wherein the anode compartment and/or the cathode compartment are closed off from their surroundings or in contact with their surroundings.

29. The reactor according to claim **21**, further comprising a component that reduces or prevents the production of methane in the anode compartment.

30. The reactor according to claim **21**, comprising an overflow.

31. A method for converting light energy into electrical energy and/or hydrogen comprising:

(a) obtaining a reactor comprising an anode compartment having an anodic material and a cathode compartment;

(b) introducing to the anode compartment, in any order,

(i) feedstock comprising an electron donor compound;

(ii) an anodophilic micro-organism capable of oxidizing the electron donor compound;

(iii) a living plant or part thereof having a root zone, wherein the root zone is placed in the anodic material; and

(b) providing light to the reactor,

wherein energy from the light is converted into electrical energy and/or hydrogen.

32. The method according to claim **31**, further comprising priming the anode compartment with a nutrient solution.

33. The method according to claim **31**, wherein the nutrient solution is a modified Hoagland nutrient solution.

34. The method according to claim **31**, further comprising filling the anode compartment with a solution.

35. The method according to claim **31**, wherein the electron donor compound is an organic compound.

36. The method according to claim **31**, wherein the plant is a plant capable of converting light energy into chemical energy.

37. The method according to claim **31**, wherein the electron donor compound is an exudate, a secretion, a lysate, vegetable matter from dead parts of plants, a gas and/or a gum of plant origin.

38. The method according to claim **31**, wherein the feedstock comprises one or more micro- and/or macronutrients.

39. The method according to claim **31**, wherein the anode compartment comprises a redox mediator.

* * * * *

US 20080213632A1

(19) United States

(12) Patent Application Publication

(10) Pub. No.: US 2008/0213632 A1

(43) Pub. Date: Sep. 4, 2008

Noguera et al.

(54) LIGHT-POWERED MICROBIAL FUEL CELLS

(76) Inventors: **Daniel R. Noguera**, Madison, WI (US); **Timothy J. Donohue**, Madison, WI (US); **Marc A. Anderson**, Madison, WI (US); **Katherine D. McMahon**, Madison, WI (US); **Isabel Tejedor**, Madison, WI (US); **Yun Kyung Cho**, Madison, WI (US); **Rodolfo E. Perez**, Madison, WI (US)

Correspondence Address:
QUARLES & BRADY LLP
33 E. MAIN ST, SUITE 900, P.O. BOX 2113
MADISON, WI 53701-2113 (US)

(21) Appl. No.: **12/029,187**

(22) Filed: **Feb. 11, 2008**

Related U.S. Application Data

(60) Provisional application No. 60/889,266, filed on Feb. 10, 2007.

Publication Classification

(51) **Int. Cl.**

H01M 8/16	(2006.01)
H01M 8/06	(2006.01)
H01M 8/02	(2006.01)

(52) **U.S. Cl.** **429/2**; 429/17; 429/19; 429/40

(57) **ABSTRACT**

Devices and methods for generating electricity utilizing a light-powered microbial fuel cell that includes a light-admitting reaction chamber containing a biological catalyst, such as a photosynthetic bacteria, in a growth medium, an anode and cathode disposed upon or within the reaction chamber, and a conductive material in electrical communication between the anode and cathode. The anode includes an oxidation catalyst, while the cathode includes a reduction catalyst that is accessible to oxygen gas. Preferably, the devices and methods utilize a single light-admitting chamber within which both cathodic and anodic reactions take place.

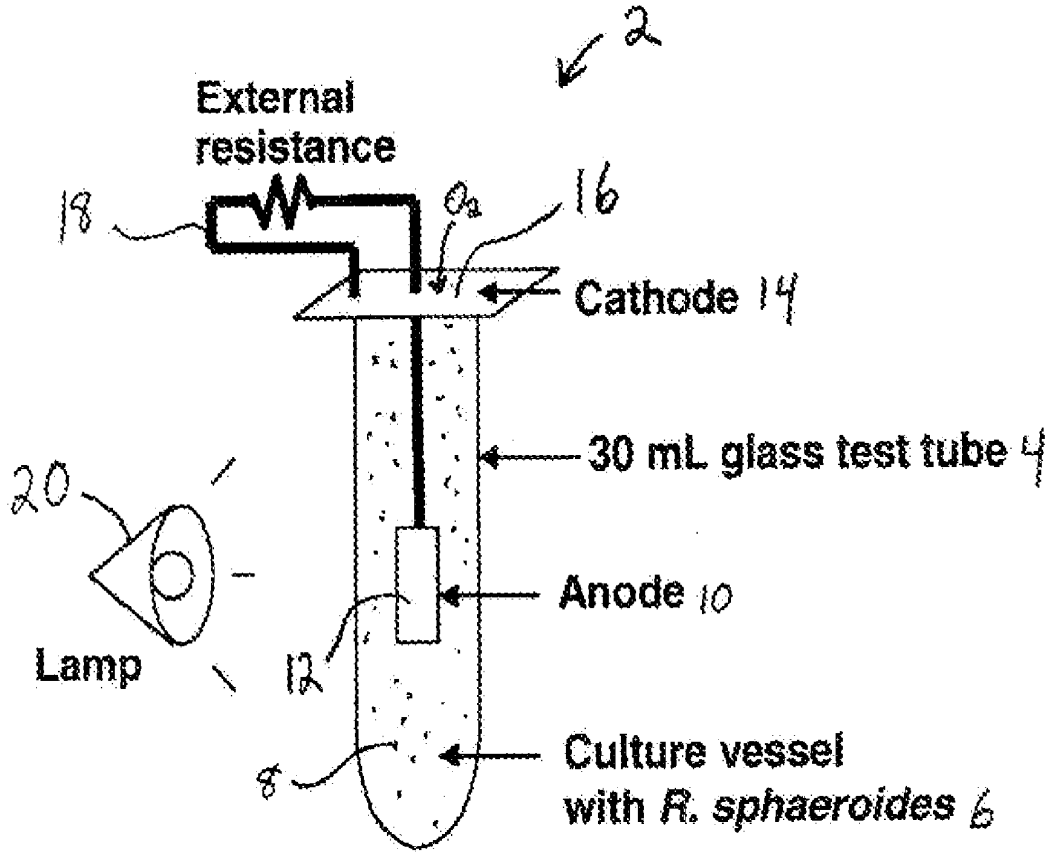
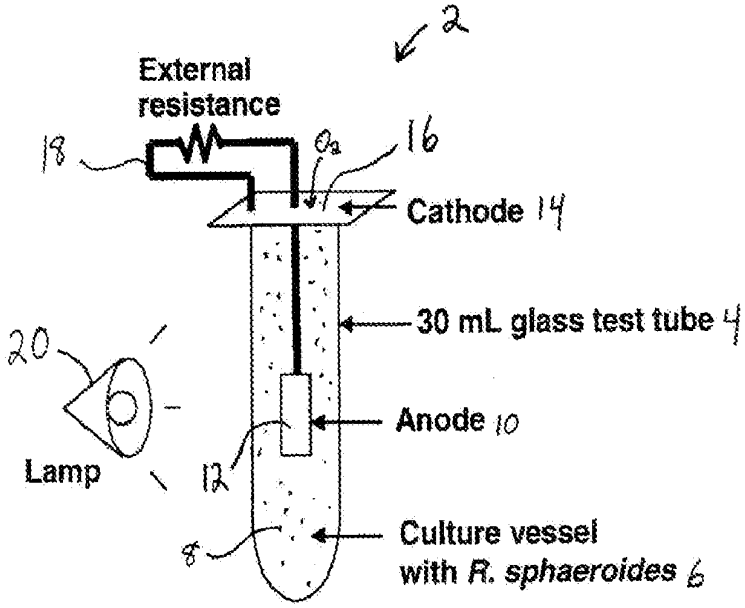


FIG. 1



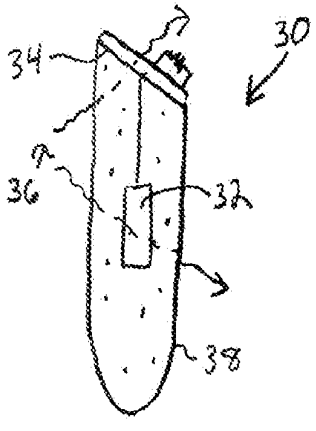


FIG. 2

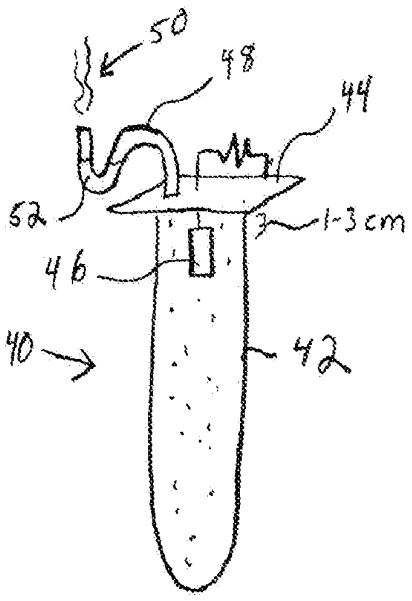


FIG. 3

FIG. 4

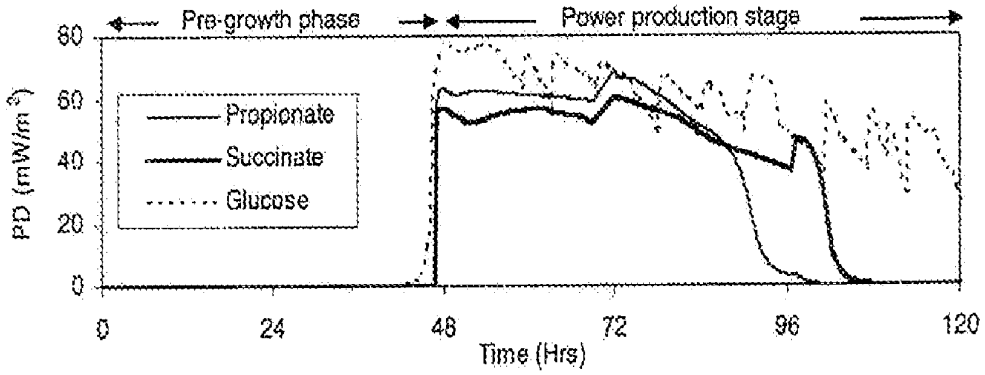


FIG. 5

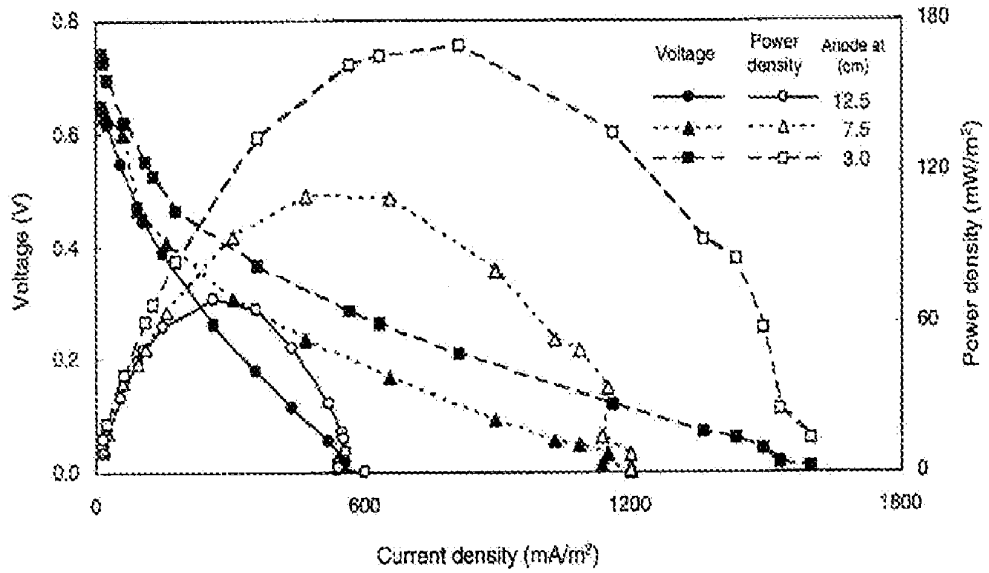
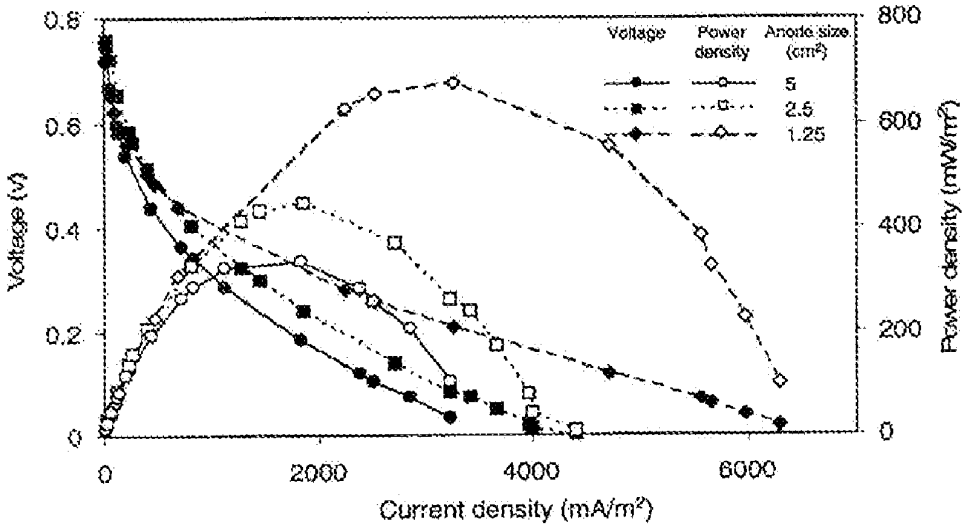


FIG. 6



LIGHT-POWERED MICROBIAL FUEL CELLS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 60/889,266, filed Feb. 10, 2007, incorporated herein by reference as if set forth in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with United States government support awarded by the following agency: DOD—NAVY Grant Nos. 144-LT10, 144-MC50, 144-QP83 and 144-QL34. The United States government has certain rights in this invention.

BACKGROUND

[0003] Alternative energy sources are being sought to offset society's dependence on fossil fuels. While many of these alternatives may be viable options in the near future, others still require major technological advances before they will make a significant impact on the overall energy budget.

[0004] One such viable alternative is solar energy (i.e., sunlight). Harvesting solar energy is a long-term, attractive strategy for meeting the global energy challenge. When compared to fossil fuels, solar energy use is a carbon-neutral process that poses no known threat from pollution or greenhouse gases. Despite these advantages, solar energy provided less than 0.1% of the world's electricity in 2001 (US Department of Energy 2005b).

[0005] Microbial fuel cells (MFCs) can be used to harvest solar energy. MFCs convert chemical energy stored in organic materials into electrical energy through a catalytic reaction mediated by photosynthetic organisms and may be an alternative to fossil fuels. With more solar energy striking the Earth in an hour (4.3×10^{20} J) than all the energy consumed on our planet in a year (4.1×10^{20} J; US Department of Energy 2005b), and with photosynthetic microbes highly adapted to capture this solar energy, technological advancements in light-powered MFCs has a potential to improve their utility in practical applications. In principle, hydrogen production via water bio-photolysis by cyanobacteria (Melis 2002) or hydrogen production via direct electron transfer to protons by photosynthetic purple non-sulfur bacteria (Gest & Kamen 1949; Koku et al. 2002) provide a source for the development of light-powered MFCs. Consequently, MFC technology is rapidly evolving for electricity generation from renewable resources.

[0006] For example, MFCs recently were shown to capture electricity from organic materials in sediments (Bond et al. 2002; Holmes et al. 2004; and Tender et al. 2002), wastewater (Liu et al. 2004; Logan 2005; and Min & Logan 2004) or agricultural wastes (Min et al. 2005). Typical MFC designs include dual-chambered cells in which anodic and cathodic chambers are separated by a proton exchange membrane (Logan et al. 2005; Park et al. 1999; and Rabaey et al. 2003); whereas more recent MFC designs include single-chambered cells in which the anode and cathode are placed within the same chamber, with the cathode in direct contact with the atmosphere (i.e., an air cathode) (Liu et al. 2005; and Liu & Logan 2004). The organisms used in these MFCs included pure cultures (Bond & Lovley 2003; and Bond & Lovley 2005) or mixed microbial communities.

[0007] Strategies are also known in which hydrogen produced in MFCs is collected before sending the collected gas to a separate MFC (He et al. 2005a). Likewise, a direct coupling of hydrogen production and electricity generation was also achieved within a MFC. In such a system, the hydrogen produced by an organism reacted at a catalytic anodic surface. Such a direct coupling has been demonstrated with dark fermentations (Niessen et al. 2005), as well as with photo-fermentations (Rosenbaum et al 2005). More recently, evidence for the presence of nanowires in cyanobacteria has also been presented (Gorby et al. 2006), suggesting the possibility of developing photosynthetic MFCs that do not depend on hydrogen production for electricity generation.

[0008] Nevertheless, MFC technology is still in its infancy, since the highest power reported for a MFC (~5,850 mW/m^2; Rosenbaum et al. 2004) is two orders of magnitude lower than the goals for conventional abiotic fuel cells (US Department of Energy 2005a). Consequently, major improvements in choice of photosynthetic organism, bio-compatible reactor configurations and electrodes are needed before any practical application of a MFC is achieved (Logan et al. 2006).

BRIEF SUMMARY

[0009] In a first aspect, the present invention is summarized as a light-powered MFC that includes a single light-admitting reaction chamber containing a photosynthetic organism in a growth medium, an anode that is conductive and catalytically active in electrical and fluid communication with a cathode, both disposed within the reaction chamber. The anode includes an oxidation catalyst, while the cathode includes a reduction catalyst that is accessible to oxygen.

[0010] The light-admitting reaction chamber can be constructed from an optically transparent material, such as glass, quartz or plastic. Optionally, the reaction chamber can include a vent for gas produced within the reaction chamber.

[0011] The photosynthetic organism is one that produces hydrogen (H_2) and can be a *Rhodospirillaceae, Acetobacteraceae, Bradyrhizobiaceae, Hyphomicrobiaceae, Rhodobiaceae, Rhodobacteraceae, Rhodocyclaceae* or *Comamonadaceae.* In particular, the photosynthetic organism can be *Rhodobacteraceae,* especially *R. sphaeroides* strain 2.4.1.

[0012] The growth medium is a growth medium for photosynthetic organisms and can include a single carbon source, such as succinate, propionate or glucose. In addition, the growth medium can be limited for a fixed nitrogen source, such as ammonia.

[0013] The anode can be carbon or graphite. Alternatively, the anode can be optically transparent and therefore can be a support material, such as glass, coated with an oxidation catalyst and a conductant, such as tin oxide, indium tin oxide, titanium dioxide or combinations thereof.

[0014] The cathode can be carbon or graphite and can be permeable to oxygen gas and nitrogen gas, such as an air cathode.

[0015] The oxidation catalyst can be platinum; whereas the reduction catalyst can be platinum, a platinum and titanium dioxide mixture, co-tetra-methyl phenylporphyrin (CoT-MPP) or iron phthalocyanine (FePc).

[0016] In a second aspect, the present invention is summarized as a method for producing electricity directly from a light-powered MFC that includes the steps of: (1) providing a MFC as described above; and (2) exposing the MFC to light, such as sunlight (i.e., solar energy). The MFC can be maintained under anaerobic and/or ammonia-limited conditions.

Because the reaction chamber is a single chamber, the photosynthetic organism can directly release hydrogen in the reaction chamber, in close proximity to the anode. Likewise, the anodic and cathodic reactions take place in the single reaction chamber.

[0017] These and other features, objects and advantages of the present invention will become better understood from the description that follows. In the description, reference is made to the accompanying drawings, which form a part hereof and in which there is shown by way of illustration, not limitation, embodiments of the invention. The description of preferred embodiments is not intended to limit the invention to cover all modifications, equivalents and alternatives. Reference should therefore be made to the claims recited herein for interpreting the scope of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. **1** is a schematic diagram of a first embodiment of the invention;

[0019] FIG. **2** is a schematic diagram of a second embodiment of the invention;

[0020] FIG. **3** is a schematic diagram of a third embodiment of the invention;

[0021] FIG. **4** depicts the power density generated in a *R. sphaeroides* photosynthetic MFC supplied with succinate, propionate or glucose;

[0022] FIG. **5** depicts the effect of the spacing between electrodes on MFC power output supplied with propionate. The center of the anode was 12.5, 7.5 or 3.0 cm from the cathode; and

[0023] FIG. **6** depicts the effect of anode size on MFC power output. The anodes were 1.25, 2.5 or 5 cm^2 strips of platinized carbon paper, with their center located 3, 1.7 and 1.1 cm away from the cathode. The carbon source used in these experiments was propionate.

[0024] While the present invention is susceptible to various modifications and alternative forms, exemplary embodiments thereof are shown by way of example in the drawings and are herein described in detail. It should be understood, however, that the description of exemplary embodiments is not intended to limit the invention to the specific forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0025] Unless defined otherwise, all technical and scientific terms as used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention pertains. Although any methods and materials similar to or equivalent to those described herein can be used in the practice or testing of the present invention, the preferred methods and materials are described herein.

[0026] As shown in FIGS. **1-3**, a light-powered MFC (**2**, **30**, **40**) includes a light-admitting reaction chamber (**4**, **38**, **42**) of any suitable geometry, such as a polygon, annulus or sphere. The reaction chamber (**4**, **38**, **42**) therefore can have a length, width, depth or circumference, depending upon the geometry. Likewise, the dimensions of the reaction chamber (**4**, **38**, **42**) will vary, depending upon the application, as laboratory settings typically require a smaller reaction chamber (**4**, **38**, **42**) than industrial settings. In a laboratory setting, such as those described in the Examples, the reaction chamber (**4**, **38**, **42**) can have volumes between about 30 ml to about 60 ml. However, in industrial settings, the reaction chamber (**4**, **38**, **42**) can have a volume of at least 1 L or more. Regardless, the reaction chamber (**4**, **38**, **42**) can be constructed of a material that allows passage of wavelengths of light in the visible to near-infrared region that are used by known or existing families of photosynthetic organisms (i.e., wavelengths from about 600 nm to about 1000 nm). Exemplary materials include, but are not limited to, glass, quartz, plastic and other optically transparent materials that allow passage of wavelengths of light in the near-infrared region. However, as would be understood by one of ordinary skill in the art, the optimal wavelength range will depend upon the photosynthetic organism being utilized within the reaction chamber (**4**, **38**, **42**).

[0027] The MFC (**2**, **30**, **40**) also includes an anode (**10**, **32**, **46**), which is an electrode through which positive electric current flows into (but electrons flow from), disposed within the reaction chamber (**4**, **38**, **42**). The anode (**10**, **32**, **46**) includes an oxidation catalyst (**12**) and optionally a conductant (i.e., an electron conductor). The anode (**10**, **32**, **46**) can be constructed of a material that is porous, such as carbon, graphite or a thin layer of conductive material coated onto an optically transparent support, such as glass. An optically transparent anode (**32**) (FIG. **2**), however, allows greater amounts of light (**36**) to pass through the reaction chamber (**38**). The efficiency of current generation of the MFCs increases when the anode (**32**) passes wavelengths of light ranging from about 600 nm to about 1000 nm. In a laboratory setting, where reaction chamber (**4**, **38**, **42**) volumes can be about 30 ml to about 60 ml, the surface area of the anode (**10**, **32**, **46**) can be about 1 cm^2 to about 10 cm^2, although one of ordinary skill in the art understands that larger surface areas per unit volume are desired. However, the location of the anode should not hinder light penetration.

[0028] The anode (**10**, **32**, **46**) includes an oxidation catalyst (**12**) disposed thereon, which can be a substance that causes or accelerates oxidation without itself being affected, thereby increasing electron transfer. A suitable oxidation catalyst (**12**) includes platinum, although other platinum metals, such as ruthenium, rhodium, palladium, osmium and iridium, can also be used. For example, the oxidation catalyst (**12**) can be platinum coated upon carbon paper, Typically, the oxidation catalyst (**12**) can be small particles of platinum deposited on a porous electron conductive support (i.e., porous carbon) heated with an ionomer, such as Nafion®. Commercially available platinum-coated anodes, such as those used in the Examples, have small particle of platinum only a few nanometers in diameter, deposited on the surface of carbon pore walls. As such, the layer of catalyst (**12**) need only be a few nanometer, but can be microns thick.

[0029] The anode (**10**, **32**, **46**) can be coated with the oxidation catalyst (**12**) though high-temperature methods and low-temperature methods known to one of ordinary skill in the art. Among high-temperature methods are sputtering and oxidation on the anode's (**10**, **32**, **46**) surface. Among low-temperature methods are sol-gel processes, liquid phase deposition and direct precipitation on the anode's (**10**, **32**, **46**) surface. See also, Park H, el al., "Effective and low-cost platinum electrodes for microbial fuel cells deposited by electron beam evaporation," Energy Fuels 21:2984-2990 (2007).

In addition, the anode (**10**, **32**, **46**) can be coated with the oxidation catalyst (**12**) by tape casting a suspension of platinized carbon.

[0030] A cathode (**14**, **34**, **44**) is in electrical and fluid communication with the anode (**10**, **32**, **46**). The cathode (**14**, **34**, **44**) is an electrode through which positive electric current flows out (but electrons flow into), disposed about the reaction chamber (**4**, **38**, **42**). The cathode (**14**, **34**, **44**) includes a reduction catalyst (**16**) and optionally a conductant (not shown). For the MFCs described herein, the cathode (**14**, **34**, **44**) can be an air cathode that is permeable to oxygen gas and nitrogen gas, but is impermeable to water. The cathode (**14**, **34**, **44**) can be constructed of a material that is porous, such as carbon or graphite. In a laboratory setting, where reaction chamber (**4**, **38**, **42**) volumes can be about 30 ml to about 60 ml, the surface area of the cathode (**14**, **34**, **44**) can be about 1 cm^2, although one of ordinary skill in the art understands that larger surface areas per unit volume are desired.

[0031] As noted above, light penetration through the MFC (**2**, **30**, **40**) can be increased by at least two ways, namely, by using an optically transparent reaction chamber (**4**, **38**, **42**) with a small diameter or by restricting the size and location of the anode (**10**, **32**, **46**) and cathode (**14**, **34**, **44**) so that they do not block light penetration. However, light penetration can also be increased by removing the cathode (**14**, **34**, **44**) from the internal volume of the reaction chamber (**4**, **38**, **42**), such as by sealing the reaction chamber (**4**, **38**, **42**) with the catalyst.

[0032] The cathode (**14**, **34**, **44**) includes a reduction catalyst (**16**) disposed thereon, which can be a substance that causes or accelerates reduction without itself being affected. Like the oxidation catalyst (**12**), the reduction catalyst (**16**) increases electron transfer. A suitable reduction catalyst (**16**) includes platinum or a platinum and titanium dioxide mixture. For example, the reduction catalyst (**16**) can be platinum coated upon carbon paper. Likewise, CoTMPP and FePc have recently been shown to be suitable alternatives to platinum in MFCs, Cheng et al. 2006b; and Zhao et al. 2005. In general, the reduction catalyst (**16**) should be accessible to atmospheric oxygen because the cathode (**14**, **34**, **44**) can be an air cathode. Alternatively, oxygen gas evolving from organisms present in the reaction chamber (**4**, **38**, **42**) may be reduced in addition to, or in lieu of, atmospheric oxygen.

[0033] The cathode (**14**, **34**, **44**) can be coated with the reduction catalyst (**16**), using any of the methods described above with the oxidation catalyst (**12**).

[0034] As shown in FIG. **3**, the MFC (**40**) may include a vent (**48**) that extends from, the cathode (**44**) or the reaction chamber (**42**) itself (not shown), which permits the emission of gas (**50**) from the inside of reaction chamber (**42**). Vent (**48**), if present, can be of a "S-shaped" variety, which means that a liquid (**52**) can be disposed within the vent (**48**) to prevent introduction of external gasses as the gas (**50**) from the inside of reaction chamber (**42**) escape to the environment. Preferably, the distance between the anode (**46**) and cathode (**44**) in this embodiment is about 1 cm to about 3 cm.

[0035] One of ordinary skill in the art, however, understands that the size of the anode (**10**, **32**, **46**) and cathode (**14**, **34**, **44**), as well as the location of the anode (**10**, **32**, **46**) relative to the cathode (**14**, **34**, **44**), will vary depending upon the volume of the reaction chamber (**4**, **38**, **42**). One of ordinary skill in the art, however, can readily determine these parameters using the teachings described below in the Examples. In general, the greater the distance between the electrodes, the greater the internal resistance of the MFC (**2**, **30**, **40**). Therefore, regardless of the size of the reaction chamber (**4**, **38**, **42**), the distance between the electrodes should be reduced as much as possible.

[0036] The anode and cathode may also include a conductant (not shown), such as, tin oxide, indium tin oxide or a combination thereof. Methods of applying conductants to these electrodes are well-known to one of ordinary skill in the art. See, e.g., U.S. Pat. No. 7,326,399. The conductant can be dispersed between the either catalyst. The layer of conductant need only about a microns or less.

[0037] The anode (**10**, **32**, **46**) and cathode (**14**, **34**, **44**) are in electrical communication via a conductive material (**18**, **39**, **54**), such as an assembly of commercially available copper/zinc wires of widths in the range of about 26 to about 30 American wire gauge (AWG) that connect each electrode through a carbon resistor having an electric resistance of 10,000 Ohms. The connections between the conductive material (**18**, **39**, **54**) and the electrodes can be of low resistance to prevent power losses in the electron flow and can be isolated using a water-proof, electrical tape such as commercial PVC tape or Kapton tape (CS Hyde; Lake Villa, Ill.). The electrical connection between the electrodes and the wires can be improved, if necessary, by using multiple conductive materials (**18**, **39**, **54**) to connect each electrode to the resistor unit, or by the sputtering of a conductive gold layer onto the electrode edges in contact with, the wires and unexposed to the growth medium.

[0038] The MFC (**2**, **30**, **40**) includes a growth medium (**8**) for culturing and growing the photosynthetic organism (**6**), as well as providing fluid communication between the anode (**10**, **32**, **46**) and cathode (**14**, **34**, **44**). The growth medium (**8**) can be any growth medium for photosynthetic organisms and should have at least a carbon source for generating electrons, nutrients and a pH compatible for such organisms. Suitable growth medium (**8**) formulations can be chemically defined and should lack potential electron acceptors, nitrates or carbon dioxide, all of which will compete for the electrons needed to support he production of hydrogen in the MFC (**2**, **30**, **40**). See, Biebl & Pfennig 1981. For example, the growth medium (**8**) can be any growth medium for photosynthetic organisms known to one of ordinary skill in the art, such as Sistrom's minimal growth medium (Sistrom 1960; and Sistrom 1962). Other suitable growth medium (**8**) formulations are known to one of ordinary skill in the art and may be used with the MFCs (**2**, **30**, **40**) described herein. See, e.g., Bergey's Manual of Systematic Bacteriology.

[0039] Although not required, one of ordinary skill in the art can increase hydrogen gas production by using a growth medium (**8**) with a single carbon source. Suitable single carbon sources are monosaccharides and organic acids, particularly those organic acids having a carboxyl group, such as monocarboxylic acids and dicarboxylic acids. See, Truper & Pfennig 1978. The single carbon source preferably has a low oxidation state (i.e., be highly reduced). Single carbon sources for use with the MFCs (**2**, **30**, **40**) described herein include, but are not limited to, succinate, propionate, glucose, pyruvate, malate, butyrate, tartrate, acetate, ethanol and glycerol.

[0040] To further increase hydrogen gas production, the growth medium (**8**) is limited for a fixed nitrogen source. That is, the ammonia in the growth medium (**8**) can be depleted by the photosynthetic organism (**6**) or can be replaced with an organic nitrogen source that limits the photosynthetic organ-

ism's (**6**) ability to produce ammonia. Alternatively, the growth medium (**8**) is essentially free of ammonia. Suitable organic nitrogen sources include, but are not limited to, amino acids such as glutamate and nitrogen gas, as well as any other fixed nitrogen that is transport or assimilated by the photosynthetic organism (**6**).

[0041] The growth medium (**8**) has a pH between about 3 to about 9, alternatively between about 5 to about 9. However, one of ordinary skill in the art understands that the optimal pH of the growth medium (**8**) for hydrogen production will vary with the isoelectic point (pI) of the materials used for the electrodes. Likewise, the pH of the growth medium (**8**) should be compatible with growth, survival or hydrogen production by the photosynthetic organism (**6**), although it is known that lower pHs may increase current production by traditional abiotic MFCs.

[0042] The photosynthetic organism (**6**) is also in the growth medium (**8**) and catalyzes the conversion of organic matter in the growth medium (**8**) into electricity by transferring electrons to a developed circuit and does so by using hydrogen as a reducing agent. One such photosynthetic organism (**6**) is purple non-sulfur bacteria, especially those from the following families: *Acetobacteraceae, Bradyrhizobiaceae, Chromatiaceae, Comamonadaceae, Hyphomicrobiaceae, Rhodobiaceae, Rhodobacteraceae, Rhodocyclaceae, Rhodospirillaceae,* as well as other known or existing photosynthetic organisms (**6**) that produce hydrogen. In addition, a mixture or consortia of these photosynthetic organisms (**6**) may be used. Of particular interest herein are members of *Rhodobacteraceae,* especially *R. sphaeroides.* Suitable *R. sphaeroides* include strains 2.4.1 (American Type Culture Collection (ATCC); Manassas, Va.; Catalog# BAA-808), 2.4.7 (ATCC: Catalog # 17028) or *R. capsidatus* B10 (ATCC; Catalog# 33303). Other photosynthetic organisms (**6**) include red, blue or green algae, as these organisms are known to produce biohydrogen.

[0043] Purple non-sulfur bacteria, such as *R. sphaeroides,* are efficient at capturing light energy (e.g., solar energy) when grown photosynthetically under anaerobic conditions and in the presence of an external organic substrate (i.e., carbon source). These organisms absorb light within the visible range, and then transform the absorbed light photosynthetically into ATP, generating electrons and protons. The electrons are eventually transferred to a high potential electron acceptor such as oxygen. These metabolic requirements are consistent with the operation of the MFCs (**2**, **30**, **40**) described herein, in which the reaction chamber (**4**, **38**, **42**) can be anaerobic for the transfer of electrons from the photosynthetic organism (**6**) to the anode (**10**, **32**, **46**), and that an external organic substrate can be provided as an electron donor to induce biological activity that fuels the MFC (**2**, **30**, **40**). The main difference with respect to typical MFCs described in the literature and the MFCs (**2**, **30**, **40**) described herein is that our reaction chambers (**4**, **38**, **42**) allow sufficient light penetration.

[0044] Manipulations of the photosynthetic organism (**6**) are also contemplated, particularly manipulations that increase hydrogen production. When *R. sphaeroides* generates excess reducing power, it passes the resulting electrons to one of several pathways (Richardson et al. 1988), such as polyhydroxybutyrate synthesis, the Calvin cycle (Paoli et al. 1998; Richaud et al. 1991; and Tichi & Tabita 2001), hydrogen gas evolution (Gest & Kamen 1949), reduction of other electron acceptors (McEwan et al. 1987) or other uncharacterized pathways (Tavano et al. 2005). Therefore, it may be possible to improve MFC (**2**, **30**, **40**) function by altering these systems.

[0045] For example, one of ordinary skill in the art may remove systems that compete for reducing power, such as carbon dioxide fixation, polyhydroxyalkanoate synthesis or production of soluble metabolites, by altering the systems that produce the hydrogen that powers the MFCs (**2**, **30**, **40**) or by eliminating the dependence of ammonia-limiting conditions (Rey et al. 2007). These alterations can be accomplished by genetic manipulation of the photosynthetic organism (**6**).

[0046] In operation, a light source (**20**, **36**) illuminates the reaction chamber (**4**, **38**, **42**), causing the photosynthetic organism (**6**) to oxidize organic substrates, such as the carbon source, and to produce electrons. Electrical current resulting from the oxidation reaction at the anode (**10**, **32**, **46**) travels to cathode (**14**, **34**, **44**) through conductive material (**18**, **39**, **54**) and is then catalytically combined by the reduction catalyst (**16**) with oxygen and protons to form water at the cathode (**14**, **34**, **44**). Thus, the photosynthetic organism (**6**) functions as a biocatalyst, mediating the degradation of organic materials to produce electrons.

[0047] Using single chambered MFCs (**2**, **30**, **40**) is important because molecular oxygen is ultimately the preferred electron acceptor. Oxygen diffusing from the cathode (**14**, **34**, **44**) (specifically, an air cathode) to the anode (**10**, **32**, **46**) dictates the minimum distance necessary between the electrodes. See, Cheng et al. 2006a. In the examples described herein, a negative effect of reducing electrode spacing was not observed. On the contrary, the best MFC performance was obtained when the center of the electrodes was separated by only 1.1 cm. Since the examples used a pure culture of *R. sphaeroides,* and *R. sphaeroides* is not know to form biofilms on electrode surfaces to date, oxygen diffusion into the MFCs was likely minimized by aerobic respiration of planktonic *R. sphaeroides* located near tire cathode.

[0048] Without intending to be limited as to the theory underlying the present invention, it is believed that the main mechanism of electron transfer from *R. sphaeroides* to the anode was through in situ oxidation of the hydrogen produced by the culture in the stationary phase, when ammonia became a limiting nutrient. Neither biogas nor electricity was produced during exponential growth. This is consistent with the general use of resting cells of purple non-sulfur bacteria for hydrogen production under ammonia-limited conditions, and observations of the kinetics of hydrogen production in growing cultures (Koku et al. 2003), which showed that hydrogen evolution did not occur until mid-exponential or stationary phase.

[0049] The rate of hydrogen production was significantly higher than the rate of in situ hydrogen utilization, and therefore, most of the hydrogen produced was vented from the MFCs. Consequently, a calculation of Coulombic efficiencies was not relevant because most of the hydrogen was vented as a biogas. To increase in situ hydrogen oxidation, one of ordinary skill in the art would typically increase the surface area of the anode per unit of reactor volume, However, the material used in the anode was based on black carbon paper, and therefore, increasing anode surface area would have resulted in a decrease in light penetration with the consequent decrease in light-driven hydrogen production. As such, the anode was made as thin as possible and located in the center of the MFC, Likewise, and from a materials science perspective, improving the efficiency of photosynthetic MFCs

required the use of anode materials that allow penetration of the near-infrared light (i.e., optically transparent) needed for photosynthesis by purple non-sulfur bacteria.

[0050] The Examples below do not show any evidence for the existence of electron transfer mechanisms other than hydrogen production and its in situ oxidation, That is, there was no observable, direct contact between the cells and anode (i.e., no nanowires were present). Likewise, very little power output (<0.01 mW/m^2) was detected when the platinum-coated anode was replaced by a similar-sized piece of plain carbon paper. Moreover, the best performance obtained corresponded to normalized power densities around 700 mW/m^2 (i.e., 2.9 W/m^3 on a volumetric basis). In contrast, MFCs incubated in tire dark produced no more than 0.5 mW/m^2 (i.e., 0.008 W/m^3 on a volumetric basis).

[0051] In the examples with commercially available platinum-coated carbon paper, we maintained high MFC performance for more than forty-eight hours, without an apparent loss in catalytic activity, thus highlighting the importance of using biocompatible materials for the light-admitting reaction chamber aid electrodes in light-powered MFCs.

[0052] The invention will be more fully understood upon consideration of the following non-limiting Examples.

EXAMPLES

Example 1

Light-Powered MFCs

[0053] Methods

[0054] MFCs. All experiments were conducted in single-chamber MFCs constructed in glass test tubes to facilitate light admittance (FIG. **1**). In the simplest configuration, an anode was submerged in a microbial culture, and a cathode sealed the top of the test tube. A slightly modified configuration used in some experiments included a side arm sealed with the cathode, while the top of the test tube was sealed with a rubber stopper. Tire typical working volumes of these MFCs were between 30 ml and 60 ml.

[0055] The anode was a rectangular piece (5 cm^2, unless noted otherwise) of either platinum-coated phosphoric acid fuel cell electrode on Toray carbon paper (0.35 mg platinum/cm^2; E-Tek; Somerset, N.J.) or plain Toray carbon paper (E-Tek) that did not contain platinum. The cathode was also made of platinum-coated Toray carbon paper (1.7 cm^2). In most experiments, the anode and cathode were connected through a 10,000 Ohm external resistance.

[0056] Biogas produced by the cultures was vented out through a needle placed at the top of the MFCs and connected to a U-shaped tube filled with a liquid (e.g., water or oil) to prevent oxygen from diffusing back into the MFCs. When necessary, sterile Sistrom's minimal medium without any organic carbon source was added to the MFCs to maintain a constant culture volume.

[0057] Photosynthetic cultures. Experiments were conducted with *R. sphaeroides* strain 2.4.1. Prior to electrochemical experiments, the bacteria were grown under anaerobic photosynthetic conditions, using Sistrom's minimal medium containing 50 mM succinate made from a succinic acid salt solution (Thermo Fisher Scientific; Waltham, Mass.) as the sole carbon source. The cultures were placed in front of an incandescent light source (10 W/m^2, as measured with a Yellow-Springs-Kettering model 6.5-A radiometer through a Coming 7-69, 620 nm to 110 nm filter) and were allowed to grow for ~2 days, until a typical red pigmentation was observed.

[0058] MFC Experiments. To initiate a MFC experiment, 1 ml of the culture was replaced with fresh Sistrom's minimal medium containing either 50 mM succinate, glucose or propionate as the carbon source, and then, the MFC was connected to the data acquisition system. To test the effect of light on function of the MFC, parallel cultures were pre-grown photosynthetically, and then amended with the carbon source, placed in the dark and monitored for power output.

[0059] Electrochemical measurements. A voltage drop across the external resistance (V) was measured and logged at five-minute intervals using a computer-controlled, digital multimeter (DMM PCI-4070; National Instruments; Austin, Tex.) combined with a data input/output card (PCI-6518, National Instruments) and a relay system that facilitated on-line measurements of up to eight MFCs operated in parallel. LabVIEW®-based software (National Instruments) was used as a graphical interface for data handling. The response variables derived from these measurements were current (I) and power (P) generated through the circuit, as well as current and power densities calculated per unit area of anode surface (A), or per unit volume of microbial culture (V_L). Current was calculated according to Ohm's law ($I=V/R$, where R is the external resistance), and power was estimated as $P=V^2/R$.

[0060] To generate polarization curves, the external circuits were disconnected, and the MFCs stabilized to an open circuit potential. Next, the external resistance was varied from 100, 000 Ohms to 10 Ohms at discrete intervals. At each condition, voltage readings were taken once the voltage drop reached an equilibrium condition, which occurred a few minutes after the replacement of the external resistance. The internal resistance in the MFCs was calculated from the slope of a linear region of the polarization curves (Logan et al. 2006).

[0061] Other analytical methods. Ammonium was measured by a salicylate method using a Test N'Tube™ Kit (Hack Loveland, Colo.). The composition of the biogas was measured by gas chromatography using a Shimadzu GC-8A system equipped with a thermal conductivity detector and a stainless steel column packed with Carbosieve SII (Supelco; Bellefonte, Pa.). Helium was used as a carrier gas, and the temperatures for the injector, column and detector were 150° C., 100° C. and 150° C., respectively.

[0062] Results

[0063] MFC power generation. FIG. **4** shows the results of typical MFC experiments, in which *R. sphaeroides* was grown photosynthetically on succinate for 18 2 days, and then power generation was measured after the reactor was supplemented with succinate, glucose or propionate. During the initial pre-growth stage, a characteristic red pigmentation developed as the bacteria grew and entered stationary phase. Usually, the power generated during this initial stage was minimal, and therefore, not routinely measured. After the addition of the carbon source to the stationary phase culture, power production and biogas formation within the MFC were observed, suggesting a correlation between biogas formation and electricity generation.

[0064] Analysis of the biogas in some MFC experiments indicated that hydrogen and carbon dioxide were the main gases produced, with hydrogen corresponding to 68% to 78% of the total. The power output slightly depended on the type of substrate added to the MFC (FIG. **4**). The resulting power density was approximately 55 mW/m^2 for MFCs supplied

with succinate, 60 mW/m^2 for MFCs supplemented with propionate, and 65 mW/m^2 for MFCs supplemented with glucose, when the external circuit included a resistor of 10,000 Ohms. These levels of power output were maintained for two to three days, until biogas production diminished. During the period of high power generation, accumulation of biogas immediately below the surface of the cathode correlated with reductions in power, and therefore, the operation of the MFCs required the periodic replacement of the volume occupied by gas with sterile medium, to maintain a good contact between the liquid and the cathode. This reduction in power was eliminated in MFCs in which the cathode was placed on the side arm of the tube, since any biogas accumulation did not interfere with the liquid-cathode contact,

[0065] MFCs placed in the dark immediately after the addition of the carbon source to the stationary phase culture resulted in insignificant power densities (less than 0.5 mW/m^2) in comparison to the power densities observed when the cultures were exposed to light. In addition, MFC experiments in the dark failed to accumulate biogas, providing further evidence for the connection between biogas production and electricity generation. It is known that light-dependent hydrogen formation occurs in *R. sphaeroides* and related photosynthetic purple non-sulfur bacteria, and that nitrogenases are one possible source of hydrogen, especially under nitrogen-limited conditions. In these MFC experiments, nitrogen became limiting by the end of the initial growth stage since the ammonium concentration decreased ~40-fold over this period (from an initial value of 3.8 mM to 0.1 mM), a condition that likely induced nitrogenase-mediated hydrogen formation when the culture received additional organic substrate.

[0066] To further explore whether hydrogen oxidation at the anode was the main mechanism of power generation in the *R. sphaeroides*-based MFCs, we performed light-exposed experiments in which the platinum-coated anode was replaced by a similar-sized piece of plain carbon paper. Under these conditions, the power output was less than 0.01 mW/m^2 (data not shown), which is insignificant compared with the power densities obtained when the anode was coated with platinum. Based on the observations that hydrogen gas was a major component of the biogas produced in these MFCs, that the increase in power density coincided with the onset of biogas production, and that power generation required the presence of a catalyst on the anode, there is strong evidence to conclude that in situ hydrogen oxidation was the major source of electrons for these light-powered MFCs.

[0067] Effect of MFC configuration on power output. To investigate the range of power densities achievable with the *R. sphaeroides*-based MFCs, experiments were conducted with varying distances between the electrodes and with electrodes differing in anode size. In single-chamber MFCs, the distance between the anode and the cathode significantly affected power output. When the electrodes are too far apart, ohmic losses restrict performance, but when they are placed too close, MFC performance can be compromised if oxygen diffusing through the cathode reaches the anode (Cheng et al. 2006a). Consequently, experiments were conducted in which the anode was placed at different distances from the cathode.

[0068] The polarization curves presented in FIG. **5** demonstrate increased power generation as the spacing between the electrodes was reduced, with a maximum power point density of 170 mW/m^2 obtained when the spacing between the center of the electrodes was 3cm and the external resistance was 510 Ohms. On a volumetric basis, the maximum power density in this configuration was 2.8 W/m^3. The gain in power output can be attributed to the decrease in the internal resistance as the spacing between electrodes was reduced. Since the shape of the polarization curves in FIG. **5** shows a clear differentiation between the slopes representative of the activation and ohmic losses (Logan et al. 2006), the internal resistance in each MFC was calculated from the slope of the linear region representing the ohmic losses. Thus, for the configuration with the largest distance between electrodes (i.e., center of electrodes was 12.5 cm apart) the internal resistance was calculated to be 1,750 Ohms, but with the smallest distance between electrodes (i.e., center of the electrodes was 3 cm apart), the internal resistance was calculated to be 510 Ohms.

[0069] The relative ratio of anode to cathode surface area also affects power generation in other MFCs (Oh & Logan 2006). The effect was demonstrated in dual chamber MFCs, where the surface area of the proton exchange membrane also had a significant impact on power output (Oh & Logan 2006). However, the effect of the surface area ratio in single chamber MFCs with air cathodes and without a proton exchange membrane has not been reported. Thus, to explore the impact of the anode to cathode surface area ratio in the power output of the single chamber light-powered MFCs, we performed experiments with anodes having surface areas of 1.25 cm^2, 2.5 cm^2 or 5 cm^2, while maintaining the surface area of the cathode constant (FIG. **6**).

[0070] In this example, the spacing between electrodes was kept as small as possible to minimize ohmic losses, as described in FIG. **5**. FIG. **6** shows that the maximum point power density in the light-powered MFCs increased as the size of the anode was reduced, suggesting that the anodic reaction was not the limiting step in these devices. The combination of the smallest anode surface and the shortest distance between the electrodes produced the best power density outputs observed so far with any light-powered MFC. The maximum power density-point obtained was 700 mW/m^2, which occurred with an external resistance of 510 Ohms. On a volumetric basis, this maximum output was 2.9 W/m^3. In addition, the internal resistance in this MFC was reduced to 130 Ohms (based on the slope of the polarization curve), which was an improvement over the internal resistance calculated from the experiments shown in FIG. **3**. These internal resistance values are orders of magnitude higher than observed in optimized MFC configurations (Cheng et at. 2006a; He et at. 2005b), suggesting that power output in light-powered MFCs could be enhanced with next generation designs that maximize proton mass transport.

[0071] The above experiments demonstrate that it is possible to operate single-chambered MFCs that capture solar energy and simultaneously utilize organic renewable resources. In our single-chambered MFCs, hydrogen was produced by *R. sphaeroides* and oxidized in situ on an anodic surface containing platinum as the catalyst. To close the circuit, an air cathode catalyzed the reduction of atmospheric oxygen. In the initial MFC designs presented here, the rate of in situ hydrogen oxidation was much lower than the rate of

hydrogen production, and therefore, most of the biogas produced was vented out of the system. In situ hydrogen oxidation could be maintained for up to forty-eight hours, without any evidence of inhibition of the electrocatalytic anodic reactions.

Example 2

Abiotic MFCs Having Optically Transparent Electrodes

[0072] Methods

[0073] MFCs. MFCs were constructed as described in Example 1; however, the MFCs had each had a different anode material: (1) platinum-coated phosphoric acid fuel cell electrode on Toray carbon paper (i.e., positive control), (2) indium tin oxide (Cardinal Glass; Spring Green, Wis.) coated on glass, (3) tin oxide (Cardinal Glass) coated on glass, (4) indium tin oxide coated on glass with a layer of titanium dioxide and platinum, and (5) tin oxide coated on glass with a layer of titanium dioxide and platinum.

[0074] Each anode had an approximate area of ~1 cm^2. Briefly, the MFCs were assembled in modified test tubes with a side window made to host a cathode. The anodes were immersed in a citric acid-phosphate buffer solution (pH 18 7). Copper tape (3M; St. Paul, Minn.) was used to enhance the area of contact between the anode and the conducting wire. The tape surrounded the top of the anode with the wire inserted in between layers of tape. This copper-based contact was then covered with insulating Kapton tape.

[0075] MFC experiments. Once the systems were assembled, hydrogen gas was delivered through a needle into the solution, to ensure hydrogen availability. The MFCs were evaluated sequentially, using the same peristaltic pump to ensure similar hydrogen flow rates. Voltage drop across a 10 kΩ resistor was measured before and during hydrogen application to each of the MFCs. The MFCs were tested under light and dark conditions.

[0076] The influence of pH on MFC performance was evaluated with the indium tin oxide anode. The MFC was modified so that the clip was replaced by conductive tape covered by insulating Kapton tape. The MFC was filled with three buffers of varying pH (3, 5 and 7). Voltage drop across a 10 kΩ resistor was measured as follows: (1) prior to hydrogen gas bubbling (2) during hydrogen gas bubbling under light conditions (3) during hydrogen gas bubbling under dark conditions, and (4) after stopping hydrogen gas bubbling.

[0077] Results

[0078] Effect of anode materials. Table 1 summarizes the voltage drop measured with the different anode materials. No significant voltage drop (i.e., less than 10 mV) was detected before starting the hydrogen bubbling. Platinized tin oxide and indium tin oxide showed promise as a material for optically transparent anodes, although its performance was lower than the platinum-coated, carbon anode. On the other hand, the tin oxide-coated glass anode did not produce any significant current flowing across the resistor. The indium tin oxide-coated glass produced some voltage drop, but at significantly lower levels than the platinum-coated anodes.

TABLE 1

Voltage Drop (in mV) in abiotic MFCs Having Different Anode Materials.

Anode Material	Voltage drop during hydrogen gas production (mV)
Platinum (positive control)	760
Indium tin oxide	102
Tin oxide	~0
Indium tin oxide + platinum + titanium dioxide	441
Tin oxide + Platinum + titanium dioxide	607

[0079] The indium tin oxide-coated anode had a power density that was somewhat lower than the positive control; whereas the tin oxide-coated anode showed negligible hydrogen generation. Both, the indium tin oxide-coated anode with a layer of titanium dioxide and platinum, and the tin oxide coated-anode with a layer of titanium dioxide and platinum had a power density that was an order of magnitude lower than the positive control.

[0080] Effects of pH on MFCs. There was an important effect of pH on MFC, and no effect of light. Tire effect of pH changes could be related with surface charge. The pI of indium tin oxide is 18 7.5, thus a less negative charge given by increasing pH might be necessary for enhancing its anodic performance. Table 2 summarizes the voltage drop of the indium tin oxide MFC at various pHs.

TABLE 2

Voltage Drop (in mV) in abiotic MFCs Exposed to Different pHs.

pH	Before hydrogen gas (mV)	During hydrogen gas (mV)	After hydrogen gas (mV)
3	4.07	14.6	7.3
5	7.5	52.3	11.2
7	0.1	115.5	7.3

[0081] The above experiments demonstrate that optically transparent electrodes are feasible for use with the MFCs described herein, that indium tin oxide by itself has conductive and reactive properties, that adding platinum to optically transparent electrodes improves their reactivity, and that indium tin oxide and tin oxide are suitable materials for optically transparent electrodes when platinum is used as a catalyst. Moreover, the above experiments demonstrate that the reaction in the MFCs is influenced by pH and may be related to the pi of the anode.

Example 3

MFCs Having Optically Transparent Electrodes

[0082] Methods

[0083] MFCs. MFC's were constructed as described in Example 2.

[0084] Photosynthetic cultures. *R. sphaeroides* strain 2.4.1 was used as the biological catalyst, as described in Example 1. However, ammonia present in the medium was replaced with an equimolar amount of glutamate.

[0085] MFC Experiments. MFC experiments were performed as described in Example 1.

[0086] Electrochemical measurements. Electrochemical measurements were performed as described in Example 1.

[0087] Results

[0088] MFC power generation. The bacteria cells grew and were not inhibited by the materials used to construct the electrodes, as evidenced by hydrogen gas production. These results indicate that the MFCs having optically transparent electrodes are indeed bio-compatible.

[0089] Effect of anode materials. The results obtained in these experiments were similar to those in Example 2. The indium tin oxide-coated glass anode showed promise as a material for optically transparent anodes, and the tin oxide-coated glass anode did not produce any significant current flowing across the resistor. When either the indium tin oxide or tin oxide anodes were coated with a thin layer of platinum/titanium dioxide, they performed similarly, with peak voltages between 70 and 80 mV. These power densities, however, where an order of magnitude lower than the positive control, which is consistent with the results obtained in Example 2.

[0090] Various changes in the details and components that have been described may be made by those skilled in the art within the principles and scope of the invention herein described in the specification and defined in the appended claims. Therefore, while tire present invention has been shown and described herein in what is believed to be the most practical and preferred embodiments, it is recognized that departures can be made therefrom within the scope of the invention, which is not to be limited to the details disclosed herein but is to be accorded the full scope of the claims so as to embrace any and all equivalent processes and products.

REFERENCES

[0091] All documents cited are incorporated herein by reference as if set forth in their entirety.

[0092] Biebl H & Pfennig N, "Isolation of members of the family *Rhodospirillaceae,*" The Prokaryotes 167-273 (Starr M, et al, eds., New York: Springer 1981).

[0093] Blankenship R, et al., "Anoxygenic Photosynthetic Bacteria." (Kluwer Academic Publishers, Boston 1995).

[0094] Bond D, et al., "Electrode-reducing microorganisms that harvest energy from marine sediments," Science 295:483-485 (2002).

[0095] Bond D & Lovley D, "Electricity production by *Geobacter sulfurreducens* attached to electrodes," Applied and Environmental Microbiology 69:1548-1555 (2003).

[0096] Bond D & Lovley D, "Evidence for involvement of an electron shuttle in electricity generation by *Geothrix fermentans,*" Applied and Environmental Microbiology 71:2186-2189 (2005).

[0097] Cheng S, et al., "Increased power generation in a continuous flow MFC with advective flow through the porous anode and reduced electrode spacing," Environmental Science & Technology 40:2426-2432 (2006a).

[0098] Cheng S, et al., "Power densities using different cathode catalysts (Pt and CoTMPP) and polymer binders (Nafion and PTFE) in single chamber microbial fuel cells," Environmental Science & Technology 40:364-369 (2006b).

[0099] Gest H & Kamen M, "Photoproduction of molecular hydrogen by *Rhodospirillum rubrum.*" Science 109:558-559 (1949).

[0100] Gorby Y, et al., "Electrically conductive bacterial nanowires produced by *Shewanella oneidensis* strain MR-1 and other microorganisms," Proceedings of the National Academy of Sciences of the United States of America 103: 11358-11363 (2006).

[0101] He D, et al., "Hydrogen photosynthesis by *Rhodobacter capsulatus* and its coupling to a PEM fuel cell," Journal of Power Sources 141:19-23 (2005a).

[0102] He Z, et al, "Electricity generation from artificial wastewater using an upflow microbial fuel cell," Environmental Science & Technology 39:5262-5267 (2005b).

[0103] Holmes D, et al., "Microbial communities associated with electrodes harvesting electricity from a variety of aquatic sediments," Microbial Ecology 48:178-190 (2004).

[0104] Kim J, et al., "Evaluation of procedures to acclimate a microbial fuel cell for electricity production," Applied Microbiology and Biotechnology 68:23-30 (2005).

[0105] Kim M, et al., "Comparison of H-2 accumulation by *Rhodobacter sphaeroides* KD131 and its uptake hydrogenase and PHB synthase deficient mutant," International Journal of Hydrogen Energy 31:121-127 (2006).

[0106] Koku H, et al., "Aspects of the metabolism of hydrogen production by *Rhodobacter sphaeroides,*" International Journal of Hydrogen Energy 27:1315-1329 (2002).

[0107] Koku H, et al., "Kinetics of biological hydrogen production by tire photosynthetic bacterium *Rhodobacter sphaeroides* OU 001," International Journal of Hydrogen Energy 28:381-388 (2003).

[0108] Lane N, "What can't bacteria do?," Nature, 441: 274-277 (2006).

[0109] Liu H, et al, "Production of electricity from acetate or butyrate using a single-chamber microbial fuel cell," Environmental Science & Technology 39:658-662 (2005).

[0110] Liu II & Logan B, "Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane,". Environmental Science & Technology 38:4040-4046 (2004).

[0111] Liu H, et al, "Production of electricity during wastewater treatment using a single chamber microbial fuel cell," Environmental Science & Technology 38:2281-2285 (2004).

[0112] Logan B, "Generating electricity from wastewater treatment," Water Environment Research, 77:211-211 (2005).

[0113] Logan B, et al, "Microbial fuel cells: methodology and technology," Environmental Science & Technology 40:5181-5192 (2006).

[0114] Logan B, et al, "Electricity generation from cysteine in a microbial fuel cell," Water Research 39:942-952 (2005).

[0115] McEwan A. et al., "The periplasmic nitrate reductase of *Rhodobacter capsulatus:* purification, characterization and distinction from a single reductase for trimethylamine-N-oxide, dimethylsulfoxide and chlorate," Archives of Microbiology 147:340-345 (1987).

[0116] Melis A, "Green alga hydrogen production: progress, challenges and prospects," International Journal of Hydrogen Energy 27:1217-1228 (2002).

[0117] Min B, ex al, "Electricity generation from swine wastewater using microbial fuel cells," Water Research 39:4961-4968 (2005).

[0118] Min B & Logan B, "Continuous electricity generation from domestic wastewater and organic substrates in a flat plate microbial fuel cell," Environmental Science & Technology 38:5809-5814 (2004).

[0119] Nandi R & Sengupta S, "Microbial production of hydrogen: an overview," Critical Reviews in Microbiology 24:61-84 (1998).

[0120] Nath K & Das D, "Improvement of fermentative hydrogen production: various approaches," Applied Microbiology and Biotechnology 65:520-529 (2004).

[0121] Niessen J, et al, "Gaining electricity from in situ oxidation of hydrogen produced by fermentative cellulose degradation," Letters in Applied Microbiology 41:286-290 (2005).

[0122] Niessen J. et at., "Exploiting complex carbohydrates for microbial electricity generation—a bacterial fuel cell operating on starch," Electrochemistry Communications 6:955-958 (2004).

[0123] Oh S & Logan **3**. "Proton exchange membrane and electrode surface areas as factors that affect power generation in microbial fuel cells," Applied Microbiology and Biotechnology 70:162-169 (2006).

[0124] Paoli G, et al., "Physiological control and regulation of the *Rhodobacter capsulatus* cbb operons," Journal of Bacteriology 180:4258-4269.

[0125] Park D, et al, "Microbial utilization of electrically reduced neutral red as the sole electron donor for growth and metabolite production," Applied and Environmental Microbiology 65:2912-2917 (1999).

[0126] Park D & Zeikus J, "Improved fuel cell and electrode designs for producing electricity from microbial degradation," Biotechnology and Bioengineering 81:348-355 (2003).

[0127] Phung N, et al., "Analysis of microbial diversity in oligotrophic microbial fuel cells using **16**S rDNA sequences," Fems Microbiology Letters 233:77-82 (2004).

[0128] Rabaey K, et al., "Microbial phenazine production enhances electron transfer in biofuel cells," Environmental Science & Technology 39:3401-3408 (2005).

[0129] Rabaey K. et al., "Biofuel cells select for microbial consortia that self-mediate electron transfer," Applied and Environmental Microbiology 70:5373-5382 (2004).

[0130] Rabaey K, et al., "A microbial fuel cell capable of converting glucose to electricity at high rate and efficiency," Biotechnology Letters 25:1531-1535 (2003).

[0131] Rabaey K & Verstraete W, "Microbial fuel cells: novel biotechnology for energy generation," Trends in Biotechnology 23:291-298 (2005).

[0132] Reguera G, et al., "Extracellular electron transfer via microbial nanowires." Nature 435; 1098-1101 (2005).

[0133] Rey F, et al., "Redirection of metabolism for biological hydrogen production," Appl. Environ. Microbiol. 73:1665-1671 (2007).

[0134] Richardson D, et al, "The role of auxiliary oxidants in maintaining redox balance during phototrophic growth of *Rhodobacter capsulatus* on proprionate or butyrate," Archives of Microbiology 150:131-137 (1988).

[0135] Riehaud P, et al., "Identification and sequence analysis of the hupR1 gene, which encodes a response regulator of the NtrC family required for hydrogenase expression in *Rhodobacter capsulatus,*" Journal of Bacteriology 173: 5928-5932 (1991).

[0136] Rosenbaum M, et al., "In situ electrooxidation of photobiological hydrogen in a photobioelectrochemical fuel cell based on *Rhodobacter sphaeroides,*" Environmental Science & Technology 39:6328-6333 (2005).

[0137] Schroder U, et al., "A generation of microbial fuel cells with current outputs boosted by more than one order of magnitude,"" Angewandte Chemie-International Edition 42:2880-2883 (2003).

[0138] Sistrom W, "A requirement for sodium in the growth of *Rhodopseudomonas sphaeroides,*" Gen Microbiol. 22:778-785 (1960).

[0139] Sistrom W, "The kinetics of the synthesis of photopigments in *Rhodopseudomonas sphaeroides,*" J. Gen. Microbiol. 28:607-616 (1962).

[0140] Tavano C. et al., "Gene products required to recycle reducing power produced under photosynthetic conditions," J. Bacterial. 187:5249-5258 (2005).

[0141] Tender L, et al., "Harnessing microbially generated power on the seafloor," Nature Biotechnology 20:821-825 (2002).

[0142] Thiele J, et al, "Control of interspecies electron flow during anaerobic-digestion—role of floe formation in syntrophic methanogenesis," Applied and Environmental Microbiology, 54:10-19 (1988).

[0143] Tichi M & Tabita F, "Interactive control of *Rhodobacter capsulatus* redox-balancing systems during phototrophic metabolism," Journal of Bacteriology 183:6344-6354 (2001).

[0144] Truper H & Pfennig N, "The photosynthetic bacteria," 19-30 (Clayton R & Sistrom W, Eds. Plenum Press, New York 1978).

[0145] Ueno Y, et al., "Microbial community in anaerobic hydrogen-producing microflora enriched from sludge compost," Applied Microbiology and Biotechnology 57:555-562 (2001).

[0146] US Department of Energy, "Annual progress report—fuel cells," (2005a) (available on the US Dept. of Energy website).

[0147] US Department of Energy, "Basic research needs for solar energy utilization," (2005b) (available on the Office of Basic Energy Sciences website).

[0148] Yagishita T, et al., "Performance of photosynthetic electrochemical cells using immobilized *Anabaena variabilis* M-3 in discharge/culture cycles," Journal of Fermentation and Bioengineering 85:546-549 (1998).

[0149] Yokoi H, et al., "Microbial hydrogen production from sweet potato starch residue," Journal of Bioscience and Bioengineering 91:58-63 (2001).

[0150] Zhao F, et al., "Application of pyrolysed iron (II) phthalocyanine and CoTMPP based oxygen reduction catalysts as cathode materials in microbial fuel ceils," Electrochem. Commun. 7:1405-1410 (2005).

[0151] Zhao F, et al., "Challenges and constraints of using oxygen cathodes in microbial fuel ceils," Environmental Science & Technology 40:5193-5199 (2006).

[0152] Zurrer H & Bachofen R, "Hydrogen Production by the Photosynthetic Bacterium *Rhodospirillum-Rubrum,*" Applied and Environmental Microbiology 37:789-793 (1979).

What is claimed is:

1. A light-powered microbial fuel cell, comprising:

a light-admitting reaction chamber containing a photosynthetic organism in a growth medium, wherein the light-admitting reaction chamber is a single reaction chamber;

an anode disposed within the reaction chamber, the anode having an oxidation catalyst disposed thereon; and

a cathode in fluid and electrical communication with the anode, wherein the cathode includes a reduction catalyst disposed thereon that is accessible to oxygen gas.

2. The microbial fuel cell of claim **1**, wherein the light-admitting reaction chamber comprises a material selected from the group consisting of glass, quartz and plastic.

3. The microbial fuel cell of claim **1**, wherein the light-admitting reaction chamber further comprises a vent for emitting a gas produced within the reaction chamber.

4. The microbial fuel cell of claim **1**, wherein the photosynthetic organism is a member selected from the group consisting of *Rhodospirillaceae, Acetobacteraceae, Bradyrhizobiaceae, Hyphomicrobiaceae, Rhodobiaceae, Rhodobacteraceae, Rhodocyclaceae* and *Comamonadaceae.*

5. The microbial fuel cell of claim **4**, wherein the Rhodobacteraceae is Rhodobacter sphaeroides.

6. The microbial fuel cell of claim **4**, wherein the *Rhodobacteraceae* is *Rhodobacter sphaeroides* strain 2.4.1.

7. The microbial fuel cell of claim **1**, wherein the growth medium comprises a single carbon source.

8. The microbial fuel cell of claim **7**, wherein the single carbon source is selected from the group consisting of succinate, propionate and glucose.

9. The microbial fuel cell of claim **1**, wherein the growth medium is limited for a fixed nitrogen source.

10. The microbial fuel cell of claim **1**, wherein the anode is selected from the group consisting of carbon and graphite.

11. The microbial fuel cell of claim **1**, wherein the anode is optically transparent.

12. The microbial fuel cell of claim **11**, wherein the anode comprises glass coated with a conductant.

13. The microbial fuel cell of claim **12**, wherein the conductant is a member selected from the group consisting of tin oxide, indium tin oxide, titanium dioxide and mixtures thereof.

14. The microbial fuel cell of claim **1**, wherein the cathode comprises a material selected from the group consisting of carbon and graphite.

15. The microbial fuel cell of claim **1**, wherein the cathode is an air cathode that is permeable to oxygen gas.

16. Tire microbial fuel cell of claim **1**, wherein the cathode is permeable to nitrogen gas.

17. The microbial fuel cell of claim **1**, wherein the oxidation catalyst is platinum.

18. The microbial fuel cell of claim **1**, wherein the reduction catalyst is selected from the group consisting of platinum titanium dioxide mixture, co-tetra-methyl phenylporphyrin (CoTMPP) and iron phthalocyanine (FePc).

19. The microbial fuel cell of claim **1**, wherein reaction chamber allows passage of wavelengths of light ranging from about 600 nanometers to about 1000 nanometers.

20. A method for producing electricity in a light-powered microbial fuel cell, comprising the steps of:

(a) providing a light-admitting reaction chamber containing in operative arrangement a photosynthetic organism in a growth medium, an anode, a cathode in electrical and fluid communication with the anode, wherein the light-admitting reaction chamber is a single chamber in which both anodic and cathodic reactions occur, and wherein the anode includes an oxidation catalyst disposed thereon and the cathode includes a reduction catalyst disposed thereon that is accessible to oxygen gas; and

(b) exposing the microbial fuel cell to light.

21. The method of claim **20**, wherein the light-admitting reaction chamber comprises a material selected from the group consisting of glass, quartz and plastic.

22. The method of claim **20**, wherein the light-admitting reaction chamber further comprises a vent for emitting a gas produced within the chamber.

23. The method of claim **20**, wherein the photosynthetic organism is a member selected from the group consisting of *Rhodospirillaceae, Acetobacteraceae, Bradyrhizobiaceae, Hyphomicrobiaceae, Rhodobiaceae, Rhodobacteraceae, Rhodocyclaceae* and *Comamonadaceae.*

24. The microbial fuel cell of claim **23**, wherein the *Rhodobacteraceae* is *Rhodobacter spharoides.*

25. The method of claim **23**, wherein the *Rhodobacteraceae* is *Rhodobacter sphaeroides* strain 2.4.1.

26. The method of claim **20**, wherein the growth medium comprises a single carbon source.

27. The method of claim **26**, wherein the single carbon source is selected from the group consisting of succinate, propionate and glucose.

28. The method of claim **20**, wherein the growth medium is limited for a fixed nitrogen source.

29. The method of claim **20**, wherein the anode comprises a material selected from the group consisting of carbon and graphite.

30. The method of claim **20**, wherein the anode is optically transparent.

31. The method of claim **30**, wherein the anode comprises glass coated with a conductant.

32. The method of claim **31**, wherein the conductant is selected from the group consisting of tin oxide, indium tin oxide, titanium dioxide and mixtures thereof.

33. The method of claim **20**, wherein the cathode comprises a material selected from the group consisting of carbon and graphite.

34. The method of claim **20**, wherein the cathode is an air cathode that is permeable to oxygen gas.

35. The method of claim **20**, wherein the cathode is permeable to nitrogen gas.

36. The method of claim **20**, wherein the oxidation catalyst is platinum.

37. The method of claim **20**, wherein the reduction catalyst is selected from the group consisting of platinum titanium dioxide mixture, co-tetra-methyl phenylporphyrin (CoTMPP) and iron phthalocyanine (FePc).

38. The method of claim **20**, wherein the light-admitting reaction chamber allows passage of wavelengths of light ranging from about 600 nanometers to about 1000 nanometers.

* * * * *

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 742 288 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
10.01.2007 Bulletin 2007/02

(51) Int Cl.:
H01M 8/16 *(2006.01)* ***H01M 4/90*** *(2006.01)*

(21) Application number: **05076560.1**

(22) Date of filing: **08.07.2005**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK YU

(71) Applicant: **UNIVERSITEIT GENT**
9000 Gent (BE)

(72) Inventors:
- **Rabaey, Korneel**
  9185 Wachtebeke (BE)
- **Verstraete, Willy**
  9032 Wondelgem (BE)

(74) Representative: **Paemen, Liesbet R.J. et al**
Bird Goen & Co
Klein Dalenstraat 42A
3020 Winksele (BE)

(54) Microbial fuel cells for oxidation of electron donors

(57) The invention relates to an improved microbial fuel cell for treatment of fluid, especially liquid streams containing a substrate or electron donor for micro-organisms which comprises a membrane (2) separating the cathode (3) and the anode (1), this membrane (2) surrounding the anode (1).

EP 1 742 288 A1

Description

[0001] The present invention relates to an improved microbial fuel cell (MFC) for treatment of fluid especially liquid streams containing a substrate or electron donor for micro-organisms as well as to method of manufacture and operation of such cells. In the technology of microbial fuel cells, micro-organisms transfer electrons gained from their substrate towards an anode, and hence enable the generation of electrical energy.

Technical Background

[0002] In MFC, micro-organisms do not directly transfer their electrons to their characteristic terminal electron acceptor, but these electrons are diverted towards an anode. The electrons are subsequently conducted over a resistance or power user towards a cathode and thus, energy from the micro-organisms is directly converted to electrical energy. To maximize the deposition of electrons on the anode and to close the electrical cycle, a proton exchange membrane is generally installed separating anode and cathode compartment. The basic design of a MFC thus comprises an anode and a cathode, separated by a proton exchange membrane.

[0003] In the article of Park, D. H., and J. G. Zeikus, 2003 "Improved fuel cell and electrode designs for producing electricity from microbial degradation", Biotechnology and Bioengineering 81:348-355, the authors describe a microbial fuel cell in which the membrane and cathode were assembled in what is referred to as a MEA, a membrane electrode assembly. This action decreased the amount of energy that was needed to operate the MFC, since aeration was no longer necessary. However, the manufacturing process of the MEA was complicated, and the electrochemical requirements for a successful MFC were not met. Moreover, overall power output remained limited to a maximal value of 788 mW/m^2, with no indication of the average value.

[0004] Simultaneously, Kim *et al.* developed a MFC in which both anode and cathode were present in one, upflow reactor, not separated by a membrane, as described in WO 03/096467 A1. The liquid stream flows through the anode towards an aerated cathode, which is located above the anode. However, this system does not produce significant current, since the internal resistance of the system is too high (in the MΩ range). Also the migration of the organic rest fraction of the liquid waste towards the cathode decreases the attainable efficiency of conversion.

[0005] In Liu, H., R. Ramnarayanan, and B. E. Logan. 2004, "Production of electricity during wastewater treatment using a single chamber microbial fuel cell", Environmental Science & Technology 38:2281-2285, the authors disclosed a tubular microbial fuel cell, in which the cathode compartment was enclosed in an inner tube, surrounded by a reactor that contains several graphite rods. This reactor was able to treat a continuous waste stream, but power output was limited to 26 mW/m^2 and the complexity of the reactor construction too high. The researchers altered the design towards a membraneless reactor in which anode and cathode were on opposite ends. While the omission of the membrane decreases the internal resistance, the distance between the electrode, the oxygen diffusion and the lack of mixing in the reactor caused a low coulombic efficiency.

[0006] Several researchers are working towards lamellar systems, in which anode and cathode are tightly junctioned, separated by a membrane. The liquid follows a specific pattern that is drawn in the electrode. This type of reactor can easily be modulated towards a stack system. However, fuel cell stacks have the disadvantage that, when one unit fails, the whole stack needs to be shut down. Moreover, the mode of operation described does not allow for large internal volume, large interphase surface between liquid and electrode, and does allow for significant oxygen intrusion towards the complete anode matrix. Furthermore, the construction of these reactors can be rather complex, and also the construction of the bipolar plate may prove to be a bottleneck. However, the decreased internal resistance does allow for higher power outputs. No data have yet been presented on the operational parameters or output of these systems.

[0007] In Schroder, U., J. Niessen, and F. Scholz, 2003, "A generation of microbial fuel cells with current outputs boosted by more than one order of magnitude", Angewandte Chemie - International Edition 42:2880-2883 the authors described anode materials based on conductive polymers, and obtained current densities of up to 1.45 mA/cm^2. This technology is also described in DE 103 15 792.

[0008] As recently disclosed in Rabaey, K., N. Boon, S. D. Siciliano, M. Verhaege, and W. Verstraete, 2004, "Biofuel cells select for microbial consortia that self-mediate electron transfer", Applied and Environmental Microbiology 70: 5373-5382, tightly matching anode and cathode did increase the power output of MFCs towards 4.31 W/m^2, in peak power and batch mode

[0009] The major bottlenecks of microbial fuel cells are the transport of electrons from the bacteria to the receiving surface, the anode, and the internal resistance of the system. To amend these bottlenecks, several solutions can be applied, such as supply of sufficient electrode surface, in order to decrease the current density and supply of mediators. In the past, redox mediators have been added to MFCs in order to facilitate the electron shuttling process. However, bacteria can also produce mediators themselves, or transfer electrons through membrane associated shuttles.

[0010] The receiving material can be altered chemically/physically to enhance electron transfer and decrease the magnitude of the overpotentials at the anode.

[0011] Construction of the reactors towards minimized internal resistance, which includes minimized distance between the electrode, minimized membrane resistance, adequate mixing

[0012] Practical design of the MFCs has thus far not focussed on high power output and ease of operation.

Summary of the Invention

[0013] It is an object of the present invention to provide an improved microbial fuel cell (MFC) for treatment of fluid especially liquid streams containing a substrate or electron donor for micro-organisms as well as to provide a method of manufacture and of operation of such cells.

[0014] Microbial fuel cells according to the present invention are able to produce electricity directly out of waste. They can achieve high power output in continuous flow mode. The presented invention describes MFCs that offer solutions for both the electron transfer bottlenecks while being a practical design.

[0015] A further advantage of the present invention is to provide microbial fuel cells with higher conversion efficiencies and rates than previously described MFCs.

[0016] Particular and preferred aspects of the invention are set out in the accompanying independent and dependent claims. Features from the dependent claims may be combined with features of the independent claims and with features of other dependent claims as appropriate and not merely as explicitly set out in the claims.

[0017] The present invention covers a microbial fuel cell for use for the treatment of aqueous substrate containing organic matter and/or electron donor, in which electrical current is generated from micro-organisms, comprising at least one reactor, each reactor comprising:

an anode able to accept electrons and to transfer them to an external circuit, and able to sustain micro-organisms;
a cathode able to transfer electrons from the external circuit to an electron acceptor or sink,
a membrane separating the cathode from the anode. The anode is three-dimensional, i.e. has a three dimensional form and is surrounded by the membrane either completely or partially. In some embodiments of the microbial fuel cells of the invention, the membrane does not completely surround the anode. The membrane can be coextensive with the cathode.

[0018] Preferably, the (membrane surface)/anode total volume) ratio is at least 1 m^2/m^3. Most preferably, the specific surface of the anode is > 50 m^2/m^3.

[0019] Several shapes may be adopted: the ensemble formed by the anode and the membrane may be tubular. The membrane may face at least two adjacent or parallel sides of the anode. The anode may comprise several sectors of coarser and finer material. The anode may include internal baffles to direct the flow of liquid through the anode.

[0020] When the anode has as a hemispherical form, the membrane may face at least 90° of the projected section of the anode. The reactor may have the global form of a mushroom, or the one of an omega.

[0021] In particularly preferred embodiments, the cathode surrounds the membrane.

[0022] In an alternative embodiment, the ensemble formed by the anode and the membrane is immerged in an aqueous body. The cathode can be placed at the surface of this aqueous body and optionally in contact with the air.

[0023] Preferably, the distance between the anode and the cathode is limited to obtain an internal resistance of maximum 50 Ω (ohms). If the internal resistance of the reactor is 50 Ω (ohms), theoretically, the attainable current output of the reactor will be maximum about 16 mA. This implies a neglectable conversion.

[0024] In a preferred embodiment, the anode is macroporous and comprises a conductive material such as graphite. The macroporous conductive anode can be formed from a particulate material such as graphite granules. The anode may consist of a three dimensional structure, with basic characteristics of a resistivity less than 1 Ω per cm (ohm per cm) material.

[0025] The cathode may comprise or consist of a graphite structure such as a textile material with carbon fibres such as a woven or knitted graphite structure. It may be moisturised with liquid containing a catalyst or mediator. Alternatively, the cathode may compose or consist of a conductive layer containing the catalyst either within the structure or on the cathode surface.

[0026] The reactor configuration may be any suitable shape, e.g. rectangular, oval, ovoid or spherical.

[0027] The fuel cells of the invention may be intended for overpressure operation in relation to environment, and further comprise means for supplying gas or gas mixtures to provide overpressure, and/or means for controlling liquid pressure valves to provide overpressure.

[0028] The membrane can be chosen from the group consisting of cation specific membranes, a proton exchange membrane, and a physical anode-cathode separator.

[0029] The microbial fuel cells of the invention may include an electron donor or electron donors for the anode selected from the group comprising or consisting of glucose, sucrose, acetate and reduced soluble present as for instance in domestic wastewater or biorefinery effluents, or a mixture thereof. The cells may comprise means for operating in upflow

mode; or in downflow mode or horizontal flow mode., and optionally may include means for backwashing.

[0030] An advantage of the present invention is that it provides a reactor design and/or a mode of operation that enables bacteria to efficiently and rapidly transfer electrons towards an insoluble electron acceptor, externally wired to a higher redox potential acceptor.

[0031] The invention can provide a high specific surface of the anode (> 50 m^2/m^3), enabling intensive contact between either bacteria or electron shuttles, and the anode. The three-dimensional structure of the anode furthermore creates a stable matrix, in which no external addition of soluble mediators is required to obtain significant power output. The membrane or separator, physically separating anode and cathode, surrounds the anode. This can enable high cation exchange rates. The cathode can either be open to the air or contacting a catalyst containing solution.

[0032] The invention can provide higher conversion rates and subsequent conversion efficiencies than previously described microbial fuel cells in continuous mode.

[0033] The invention provides better technological solutions to apply and practically design microbial fuel cells.

[0034] The invention is capable of using a wide variety of substrates as feed, varying from carbohydrates such as glucose, sucrose, acetate to mixed substrates such as domestic wastewater and biorefinery effluents.

[0035] The invention is capable of efficiently biodegrading substrates delivered in the incoming fluid.

[0036] The above and other characteristics, features and advantages of the present invention will become apparent from the following detailed description, taken in conjunction with the accompanying drawings, which illustrate, by way of example, the principles of the invention. This description is given for the sake of example only, without limiting the scope of the invention.

Brief Description of the drawings

[0037] The reference figures quoted below refer to the attached drawings.

Fig. 1A and Fig. 1B illustrate a view of the tubular microbial fuel cell used for the experiments in accordance with embodiments of the present invention. Fig. 1A: Scheme ; Fig. 1B: Overall set-up.

Fig. 2 illustrates another embodiment of a microbial fuel cell according to the present invention, wherein the reactor has the form of a mushroom.

Fig. 3 illustrates still another embodiment of a microbial fuel cell according to the invention, wherein the reactor is submerged in an aqueous body and has the form of an omega.

Fig. 4. is a graph showing the evolution of the amount of COD removed as electricity in function of the COD loading rate for a glucose fed tubular reactor. The external resistances applied were 50 Ω (ohms) (♦) and 25 Ω (ohms) (■). Upon a further decrease of the external resistance to 10 Ω (ohms), the amount of COD converted to current increased to 0.92 kg COD m^{-3} d^{-1}.

Fig. 5 is a graph showing the evolution of the power output, in W/m^3 of anode liquid volume, for an acetate fed microbial fuel cell according to an embodiment of the present invention.

Fig. 6 is a graph showing the evolution of the amount of COD removed as electricity in function of the COD loading rate for an acetate fed tubular reactor. The external resistances applied were 20 Ω (ohms) (♦) and 10 Ω (ohms) (■).

[0038] In the different figures, the same reference signs refer to the same or analogous elements.

Detailed Description of the illustrative embodiments

[0039] The present invention will be described with respect to particular embodiments and with reference to certain drawings but the invention is not limited thereto but only by the claims. Any reference signs in the claims shall not be construed as limiting the scope. The drawings described are only schematic and are non-limiting. In the drawings, the size of some of the elements may be exaggerated and not drawn on scale for illustrative purposes. Where the term "comprising" is used in the present description and claims, it does not exclude other elements or steps. Where an indefinite or definite article is used when referring to a singular noun e.g. "a" or "an", "the", this includes a plural of that noun unless something else is specifically stated.

[0040] Furthermore, the terms first, second, third and the like in the description and in the claims, are used for distinguishing between similar elements and not necessarily for describing a sequential or chronological order. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other sequences than described or illustrated herein.

[0041] Moreover, the terms top, bottom, over, under and the like in the description and the claims are used for descriptive purposes and not necessarily for describing relative positions. It is to be understood that the terms so used are interchangeable under appropriate circumstances and that the embodiments of the invention described herein are capable of operation in other orientations than described or illustrated herein.

[0042] The present invention provides a microbial fuel cell for use for the treatment of organic matter and electron donors, in which electrical current is generated from micro-organisms, comprising at least one reactor, each reactor comprising:

- an anode able to accept electrons and to transfer them to an external circuit, and able to sustain micro-organisms;
- a cathode able to transfer electrons from the external circuit to an electron acceptor or sink,
- a membrane separating the cathode from the anode.

The anode is three-dimensional and is either completely or partially surrounded by the membrane, e.g. at least 40%, 50%, 70% or 90% surrounded. The anode is macroporous, e.g. it can be formed of a particulate material. The cathode and membrane can be coextensive.

[0043] The substrate can be an aqueous mixture of water and organic waste and/or electron donor. The invention consists of a reactor design and/or a mode of operation that enables bacteria to efficiently and rapidly transfer electrons towards an insoluble electron acceptor, externally wired to a higher redox potential acceptor. A high specific surface of the anode (> 50 m^2/m^3), enables intensive contact between either bacteria or electron shuttles, and the anode. The three-dimensional structure of the anode furthermore creates a stable matrix, in which no external addition of soluble mediators is required to obtain significant power output. The three dimensional structure of the anode can take any suitable cross-section or shape. The membrane or separator, physically separating anode and cathode, at least partly surrounds the anode. This can enable high cation exchange rates. The cathode can either be open to the air or contacting a catalyst containing solution. The (membrane surface)/(anode volume) ratio is preferably at least 1 m^2/m^3.

Examples

Example 1

[0044] A microbial fuel cell (MFC) as illustrated in Fig. 1A and 1 B was operated on glucose containing influent in duplicate. The inner part of the reactor is filled with a conductive packing, e.g. conductive particles or granules, namely a graphite material such as graphite granules (type 0514, average diameter 4 mm, porosity of 0.53, Le Carbone, Belgium). These graphite granules function as an anodic electrode matrix and constitute the anode 1 of the MFC. The anode has a three-dimensional shape, e.g. tubular or cylindrical or rod-like. The dimensions of the reactor are 200 mm high and 46 mm breadth.

[0045] The membrane 2 surrounds the anode 1, and the cathode 3 surrounds the membrane 2. Electrical contact is foreseen over an external load 4. The reactor was inoculated with a bacterial consortium enriched in an MFC, e.g. according to Rabaey, K., N. Boon, S. D. Siciliano, M. Verhaege, and W. Verstraete, 2004, "Biofuel cells select for microbial consortia that self-mediate electron transfer", Applied and Environmental Microbiology 70:5373-5382.

[0046] The membrane 2 is a cation exchange membrane dimension of 12.7(1) x 20.0(h) cm (Ultrex ™CMI-5000, Membranes International Inc.). The free liquid volume was 210 ml. 720 ml of feeding liquid or influent was provided daily, with a basic composition of (composition per litre): 6 g Na_2HPO_4; 1 g NH_4Cl; 0.5 g NaCl; 0.2465 g $MgSO_4.7H_2O$; 3 g KH_2PO_4; 14.7 g $CaCl_2$. To this basic medium, 1 ml per litre influent of a trace element solution was added (composition per litre trace element solution): $FeSO_4.7H_2O$ 1g; $ZnCl_2$ 70 mg; $MnCl_2.4H_2O$ 100 mg; H_3BO_3 6 mg; $CaCl_2.6H_2O$ 130 mg; $CuCl_2.2H_2O$ 2 mg; $NiCl_2.6H_2O$ 24 mg; $Na_2Mo_4.2H_2O$ 36 mg; $CoCl_2.6H_2O$ 238 mg. Glucose was added to this medium to obtain respective loading rates of 0.5, 1.1, 1.6 and 2.7 kg glucose-COD per m^3 anode liquid volume per day. The operation was repeated once.

[0047] Fig. 1 B illustrates the over-all set up of the MFC. The influent 5 was injected into the anode 1 via the anode loop 6 represented at the right side of Fig. 1B. After passing through the reactor, the liquid was evacuated under the form of an effluent 7. Black arrows represent circulation of the liquid treated through the MFC.

[0048] The cathode 3 consisted of a hexacyanoferrate (50 mM) solution sprinkled woven graphite mat with the same dimensions as the membrane 2. This solution used as catholyte 7 entered into the reactor via the cathode loop 8. The catholyte 7 was ejected after use and recycled.

[0049] The experiment was carried out with several microbial fuel cells at the same time. Voltage over the MFC was monitored continuously. By applying different external resistances as loads different power outputs could be obtained for similar loading rates, as can be seen on Fig. 4. The reactors generated up to 66 W of average daily power per m^3 of anode liquid volume (Table 1). This corresponds to high coulometric, energetic and COD-removal efficiencies.

Table 1. Results obtained using tubular type reactors fed with glucose, acetate and domestic sewage.

Substrate	Av. (Max.) Power (W m^{-3})	Av. (Max.) CE (%)	Av. (Max.) Substrate to Current (kg COD m^{-3} d^{-1})*	Losses to sulphate (kg COD m^{-3} d^{-1})*
Acetate	52 ± 10 (90)	87 ± 9 (98)	0.79 ± 0.08 (1.12)	0.002 ± 0.005
Glucose	49 ± 8 (66)	43 ± 9 (74)	0.69 ± 0.06 (0.92)	0.243 ± 0.009
Wastewater	8 ± 5 (48)	22 ± 5 (36)	0.43 ± 0.10 (0.69)	0.086 ± 0.024

CE: Coulombic efficiency; Av.: Average; Max.: Maximum; * Expressed per anode liquid volume

[0050] Up to 2.26 kg COD was removed per m^3 anode liquid volume per day. The lower the loading rate in glucose, the higher the ratio produced current/loading rate (COD converted to current/COD supplies) becomes, yielding conversion efficiencies (coulombic) of up to 90%.

Example 2

[0051] The same type of reactor was operated as for example 1 on acetate containing influent (Fig 5). Same mode of operation as example 1 was performed, with acetate as carbon source, at several loading rates. The power output was, on average, 52 W/m^3, with a maximum of 87 W/m^3. This corresponded with almost full coulombic conversion of the COD to current. Again, the attained COD removal varied in function of COD loading. (Fig 6)

Example 3

[0052] A tubular reactor similar to that of examples 1 and 2 was operated on domestic wastewater, in a similar manner to that of the set-ups of example 1 and 2, with 0.72 litre of domestic wastewater as feeding per reactor per day. The power output was, on average, 8 W/m^3, with a maximum of 48 W/m^3 (Table 1). This corresponded with almost full coulombic conversion of the COD that was removed out of the influent to current.

Example 4

[0053] The microbial fuel cell used in this example is an MFC having the global shape of a mushroom, which is illustrated schematically in Fig. 2. Electric contacts over a load can be foreseen to branch anode and cathode (electric circuitry not shown). Influent passes through an anode matrix with different sectors of coarser and finer material, in order to selectively trap particles present in the influent that could impair functioning of the reactor. Conductive separators can be used to separate coarser and finer electrode fractions.

[0054] The anode 10 is three-dimensional and has a matrix structure. The influent 11 enters in the MCF via an inlet 12 which forms part of the basis of the structure. The liquid circulates into the reactor according to directions represented schematically by the black arrows. It first enters in a first compartment of the anode filled with coarse conductive packing 13 consisting of graphite. Large non-degradable particles such as sand are captured into a collector 14. The liquid then flows to the two following compartments of the anode, filled with medium conductive packing 15 consisting of graphite. It enters the last compartment of the anode filled with fine conductive packing 16. Baffles 17 distributed in between the compartments guide the liquid movement. Conductive packing can be a particulate conductive material such as graphite granules of various diameters according to influent characteristics and effluent requirements. Also conductive grids, mats or frameworks can be used, or any conductive material allowing flow through of the liquid and growth of the biocatalyst, e.g. a macroporous conductive material.

[0055] The liquid leaves the anode 10 through a conduit bounded on the one hand by the membrane 18 surrounded by the cathode 19, and on the other hand by a conductive separator 20 defining the anode 10. Eventually, the liquid leaves the reactor in the form of effluent 21 via the outlet 22.

[0056] In this embodiment, the membrane 18 does not completely surround the anode 10 Instead it surrounds the anode to about 60%. The membrane 18 is coextensive with the cathode. Hence the membrane separates the anode from the cathode.

Example 5

[0057] The microbial fuel cell used in this example is an MFC having the global shape of an omega, which is illustrated schematically in Fig. 3. Electrical contacts connected via a load can be foreseen to branch the anode and cathode (electrical circuitry not shown).

[0058] As in the previous examples, the membrane 23 surrounds the anode 24. The latter is conceived in a way that it can be constructed supported by environmental hydrostatic water pressure. The membrane separates the anode from the cathode. The cathode 25 can be positioned at the top of a water body 26 and contacts the air. This reduces the structural requirements of the reactor materials. In the anode 24, the reactor can operate according to the reactors described in accordance with any of the examples 1 or 4. The influent 27 enters through the inlet 28, circulates into the reactor and the treated liquid leaves it as en effluent 29 via outlet 30. The flow within the anode may be guided by means of internal baffles so that the liquid is guided throughout the anode. The anode may also be made up of various compartments with different conductive materials in the various compartments, e.g. finer or coarser granules, such as graphite granules.

[0059] Other arrangements for accomplishing the objective of the microbial fuel cells embodying the invention will be obvious for those skilled in the art.

[0060] It is to be understood that although preferred embodiments, specific constructions and configurations, as well as materials, have been discussed herein for devices according to the present invention, various changes or modifications in form and detail may be made without departing from the scope and spirit of this invention.

Claims

1. Microbial fuel cell for use for the treatment of aqueous substrate containing organic matter and/or electron donor, in which electrical current is generated from micro-organisms, comprising at least one reactor, each reactor comprising

   - an anode (1; 10; 24) able to accept electrons and to transfer them to an external circuit, and able to sustain micro-organisms;
   - a cathode (3; 19; 25) able to transfer electrons from the external circuit to an electron acceptor or sink,
   - a membrane (2; 18; 23), separating the cathode (3) from the anode (1),

   wherein

   - the anode is three-dimensional and surrounded at least partly by the membrane (2).

2. Microbial fuel cell according to claim 1, wherein the (membrane surface/anode total volume) ratio is at least 1 m^2/m^3.

3. Microbial fuel cell according to any of the previous claims, wherein the surface of the anode is > 50 m^2/m^3.

4. Microbial fuel cell according to any of the previous claims, wherein the ensemble formed by the anode (1) and the membrane (2) is tubular.

5. Microbial fuel cell according to any of the previous claims, wherein the membrane (2) faces at least two adjacent or parallel sides of the anode (1).

6. Microbial fuel cell according to any of the previous claims, wherein the anode (10) comprises several sectors of coarser and finer material.

7. Microbial fuel cell according to any of the claims 1 to 3, wherein the anode has an hemispherical form and in that the membrane (18) faces at least 90° of the projected section of the anode (10).

8. Microbial fuel cell according to any of the previous claims, wherein the reactor has the global form of a mushroom.

9. Microbial fuel cell according to any of the claims 1 to 7, wherein that the reactor has the global form of an omega.

10. Microbial fuel cell according to any of the previous claims, wherein the cathode (3; 19) surrounds the membrane (2; 18).

11. Microbial fuel cell according to any previous claim, wherein the ensemble formed by the anode and the membrane is immersed in a water body (26) and wherein the cathode (25) is placed at the surface of this water body and contacts the air.

12. Microbial fuel cell according to any of the previous claims, wherein the membrane (18, 24) completely surrounds the anode (10; 23).

13. Microbial fuel cell according to any of the previous claims, wherein the distance between the anode and the cathode is limited to obtain an internal resistance of maximum 50 Ω (ohms).

14. Microbial fuel cell according to any of the previous claims, wherein the anode (1; 10; 24) comprises a macroporous particulate material.

15. Microbial fuel cell according to any of the previous claims, wherein the anode (1; 10; 24) consists of a three dimensional structure, with a resistivity of less than 1 Ω per cm (ohm per cm) of material.

16. Microbial fuel cell according to any of the previous claims, wherein the cathode consists of a textile conductive structure moisturized with liquid containing catalyst or mediator.

17. Microbial fuel cell according to any of the claims 1 to 15, wherein the cathode consists of a conductive layer containing the catalyst either within the structure or on the cathode surface.

18. Microbial fuel cell according to any of the previous claims for in flow through operation, wherein the reactor configuration is rectangular, ovoid or spherical.

19. Microbial fuel cell according to any of the previous claims, wherein it is adapted for overpressure operation in relation to the environment, and in that it further comprises means for supplying gas or gas mixtures to provide overpressure,

20. Microbial fuel cell according to any of the previous claims, wherein it is adapted for overpressure operation in relation to the environment, and in that it further comprises means for controlling liquid pressure valves to provide overpressure.

21. Microbial fuel cell according to any of the previous claims, wherein the membrane is chosen from the group consisting of cation specific membranes, a proton exchange membrane, or physical anode-cathode separator.

22. Microbial fuel cell according to any of the previous claims, comprising an electron donor or electron donors for the anode selected from the group comprising glucose, sucrose, acetate and reduced soluble present as for instance in domestic wastewater or biorefinery effluents, or a mixture thereof.

23. Microbial fuel cell according to any of the previous claims, comprising means for operating in upflow mode; or in downflow mode or horizontal flow mode.

24. Microbial fuel cell according to any of the preceding claims comprising means for backwashing,

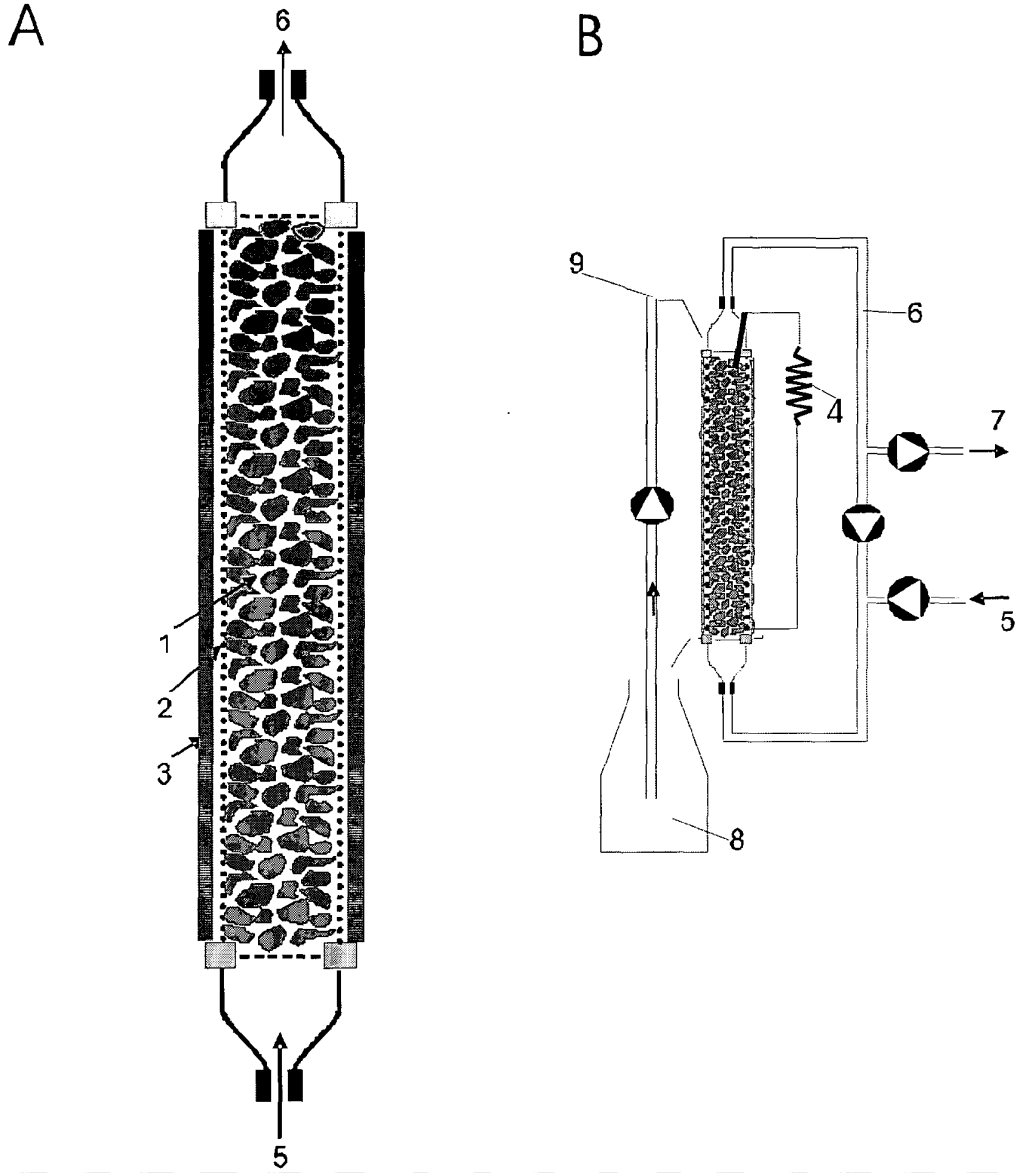


Figure 1

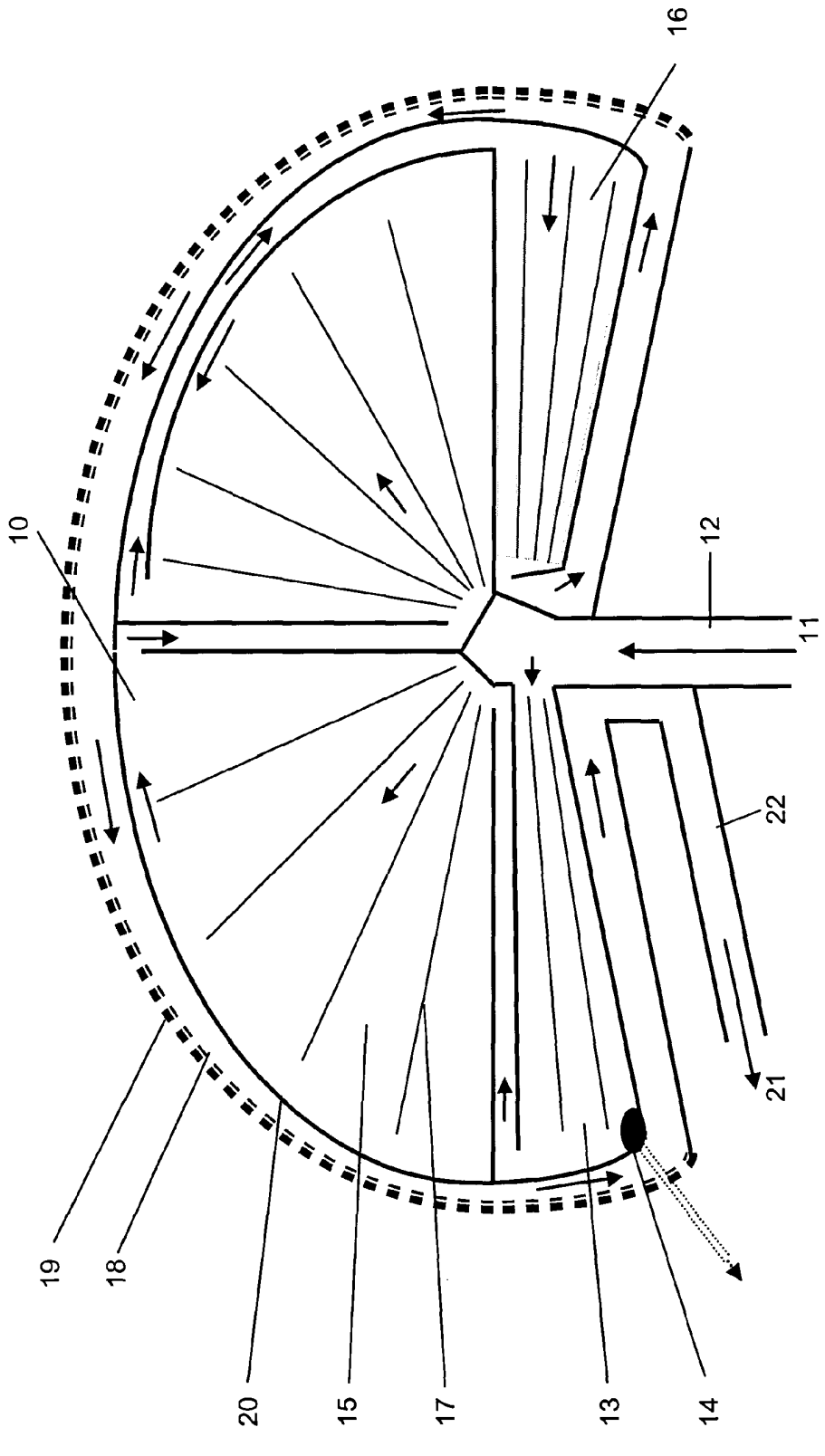


Figure 2

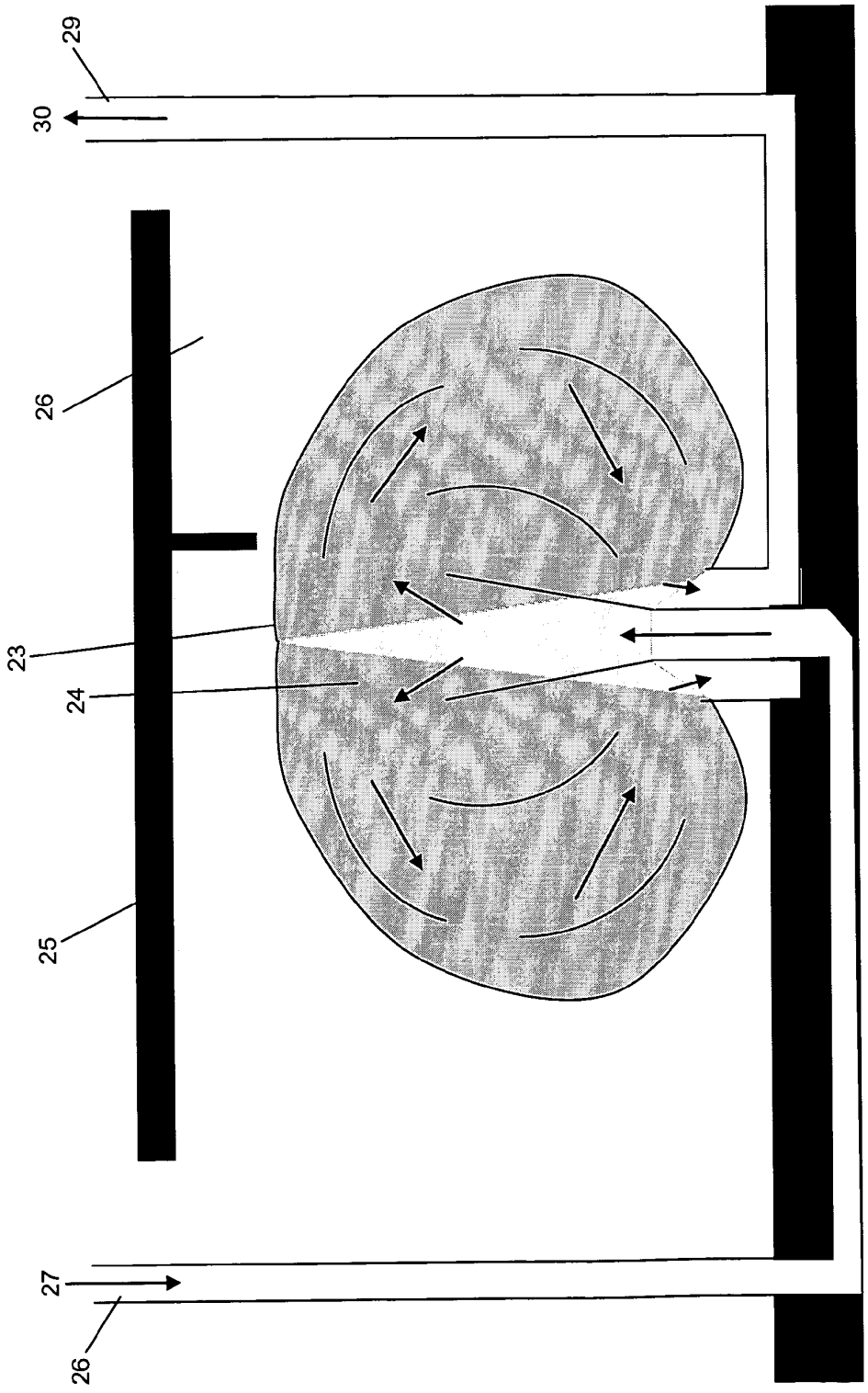


Figure 3

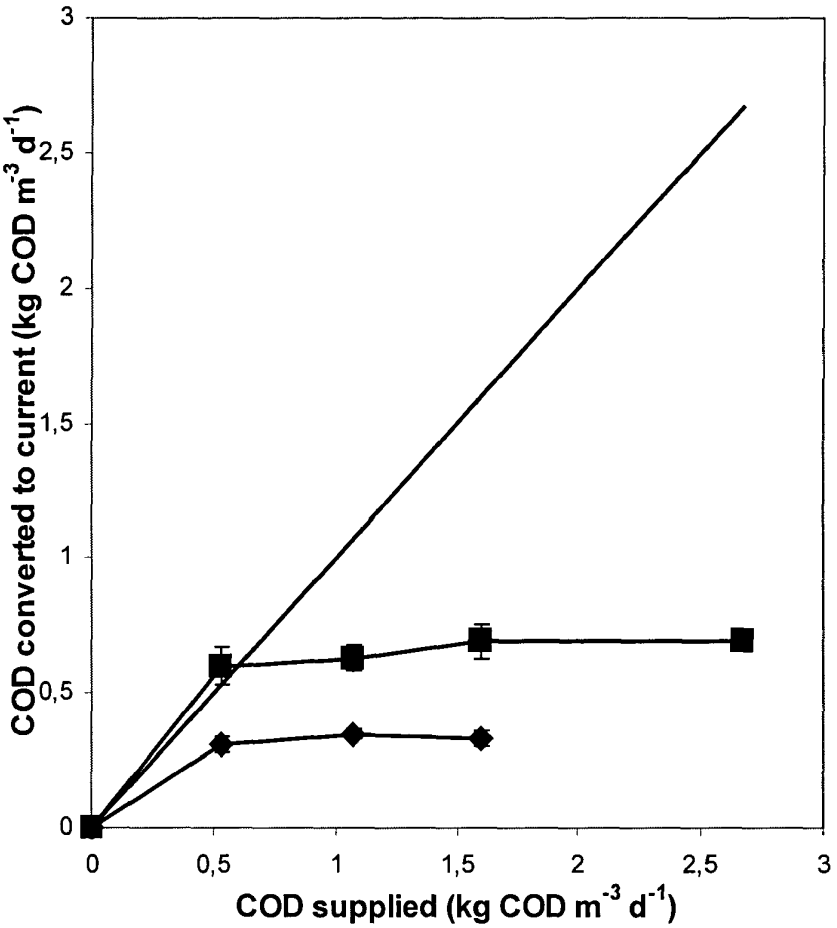

COD converted to current (kg COD m-3 d-1)
COD supplied (kg COD m-3 d-1)
0
0,5
1
1,5
2
2,5
3

Figure 4

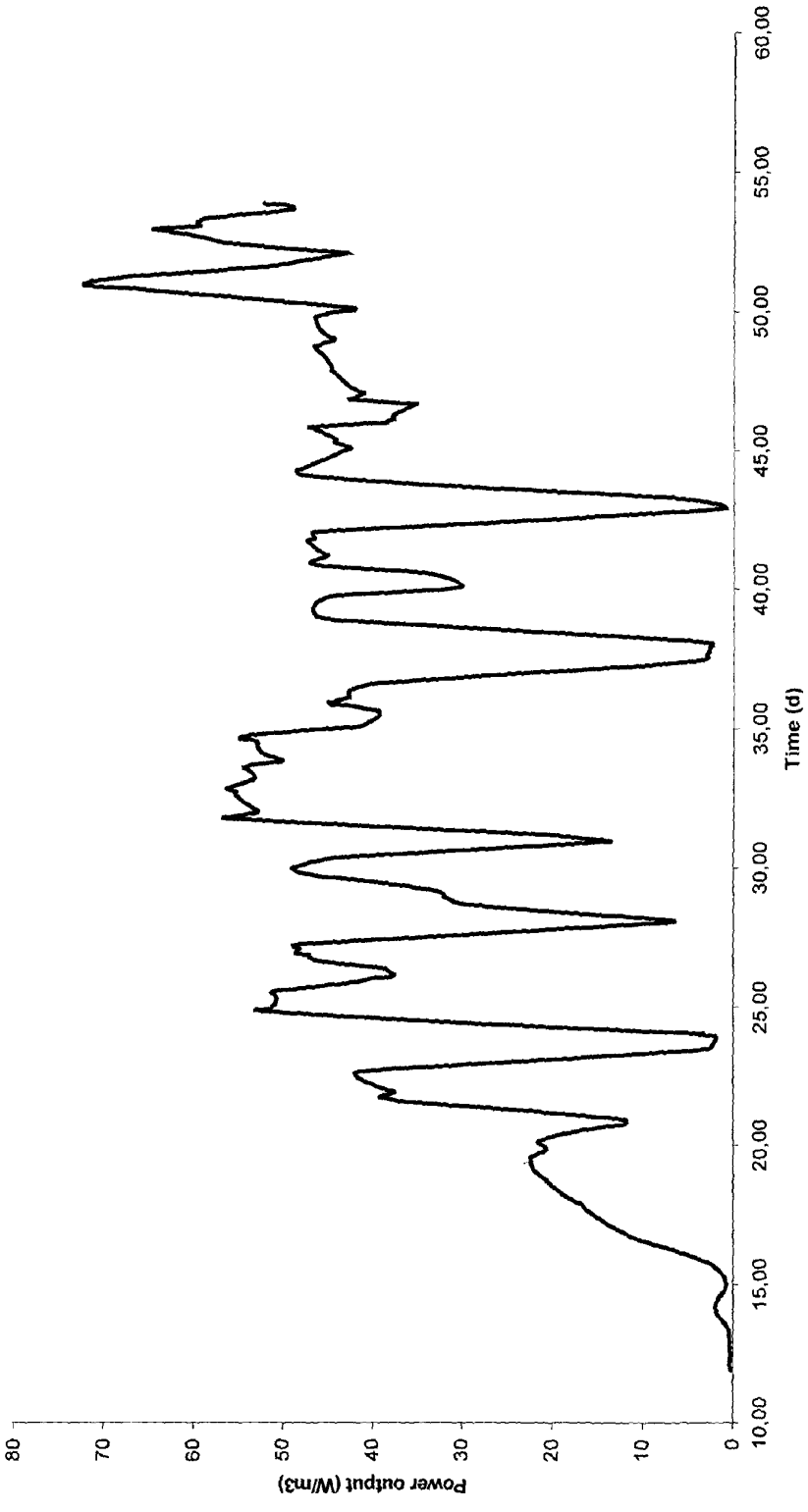

Power output (W/m3)
0
10
20
30
40
50
60
70
80
10,00
15,00
20,00
25,00
30,00
35,00
40,00
45,00
50,00
55,00
60,00
Time (d)

Figure 5

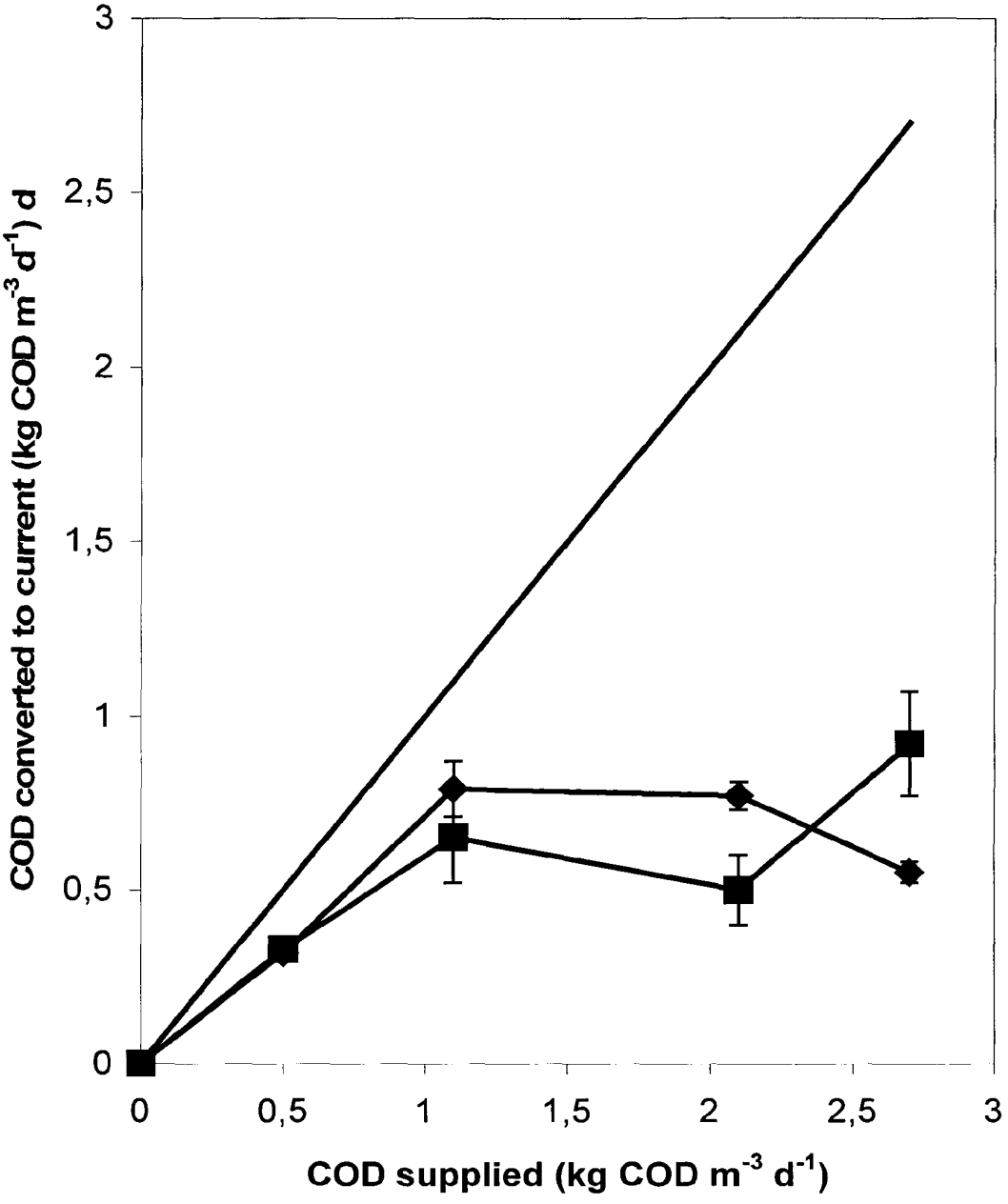

COD converted to current (kg COD m-3 d-1) d
COD supplied (kg COD m-3 d-1)
0
0,5
1
1,5
2
2,5
3

Figure 6

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 07 6560

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	RABAEY K ET AL: "Microbial fuel cells: novel biotechnology for energy generation" TRENDS IN BIOTECHNOLOGY, ELSEVIER PUBLICATIONS, CAMBRIDGE, GB, vol. 23, no. 6, June 2005 (2005-06), pages 291-298, XP004910207 ISSN: 0167-7799 * the whole document * * table 2 * * page 294, right-hand column, paragraph 2 - page 295, left-hand column, paragraph 3 * * figure 3 *	1-24	H01M8/16 H01M4/90
D,A	H.LIU AND AL: "Production of electricity during wastewater treatment using a single chamber microbial fuel cell" ENVIRONMENTAL SCIENCE & TECHNOLOGY, vol. 38, 2004, pages 2281-2285, XP002360453 * the whole document *	1-24	
D,A	U. SCHÖDER AND AL: "A generation of microbial fuel cells with current outputs boosted by more than one order of magnitude" ANGEWANDTE CHEMIE-INTERNATIONAL EDITION, vol. 42, 2003, pages 2880-2883, XP002360454 * the whole document *	1-24	TECHNICAL FIELDS SEARCHED (IPC) H01M C12M C12Q
D,A	WO 03/096467 A (KOREA INSTITUTE OF SCIENCE AND TECHNOLOGY; KIM, BYUNG HONG; CHANG, IN) 20 November 2003 (2003-11-20) * page 2, line 28 - page 3, line 20 * * page 4, line 22 - page 5, line 23 * * page 7, line 9 - page 8, line 6 * * figure 1 *	1-24	

-/--

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	21 December 2005	Gamez, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 05 07 6560

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	US 2004/241528 A1 (CHIAO MU ET AL) 2 December 2004 (2004-12-02) * figure 2 * * page 2, paragraph 29 - paragraph 39 * * page 3, paragraph 42 - paragraph 45 * * page 4, paragraph 52 - paragraph 63 * * page 6 - page 106 *	1-24	
A	US 2004/241771 A1 (ZEIKUS JOSEPH GREGORY ET AL) 2 December 2004 (2004-12-02) * the whole document *	1-24	
A	IEROPOULOS I A ET AL: "Comparative study of three types of microbial fuel cell" ENZYME AND MICROBIAL TECHNOLOGY, STONEHAM, MA, US, vol. 37, no. 2, 1 July 2005 (2005-07-01), pages 238-245, XP004889710 ISSN: 0141-0229 * the whole document *	1-24	
			TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	21 December 2005	Gamez, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 05 07 6560

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

21-12-2005

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 03096467 A	20-11-2003	AU 2003230342 A1	11-11-2003
		CN 1659734 A	24-08-2005
		KR 2003088263 A	19-11-2003
		US 2005208343 A1	22-09-2005
US 2004241528 A1	02-12-2004	NONE	
US 2004241771 A1	02-12-2004	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 03096467 A1 **[0004]**
- DE 10315792 **[0007]**

Non-patent literature cited in the description

- **PARK, D. H. ; J. G. ZEIKUS.** Improved fuel cell and electrode designs for producing electricity from microbial degradation. *Biotechnology and Bioengineering,* 2003, vol. 81, 348-355 **[0003]**
- **LIU, H. ; R. RAMNARAYANAN ; B. E. LOGAN.** Production of electricity during wastewater treatment using a single chamber microbial fuel cell. *Environmental Science & Technology,* 2004, vol. 38, 2281-2285 **[0005]**
- **SCHRODER, U. ; J. NIESSEN ; F. SCHOLZ.** A generation of microbial fuel cells with current outputs boosted by more than one order of magnitude. *Angewandte Chemie - International Edition,* 2003, vol. 42, 2880-2883 **[0007]**
- **RABAEY, K. ; N. BOON ; S. D. SICILIANO ; M. VERHAEGE ; W. VERSTRAETE.** Biofuel cells select for microbial consortia that self-mediate electron transfer. *Applied and Environmental Microbiology,* 2004, vol. 70, 5373-5382 **[0008] [0045]**

US 20120082868A1

(19) **United States**

(12) **Patent Application Publication**

Huang et al.

(10) **Pub. No.: US 2012/0082868 A1**

(43) **Pub. Date: Apr. 5, 2012**

(54) **FLOATING MICROBIAL FUEL CELLS**

(75) Inventors: **Yuelong Huang**, Gainesville, FL (US); **Zhen He**, Bayside, WI (US); **Florian Mansfeld**, Los Angeles, CA (US)

(73) Assignee: **UNIVERSITY OF SOUTHERN CALIFORNIA**, Los Angeles, CA (US)

(21) Appl. No.: **13/250,939**

(22) Filed: **Sep. 30, 2011**

Related U.S. Application Data

(60) Provisional application No. 61/389,104, filed on Oct. 1, 2010.

Publication Classification

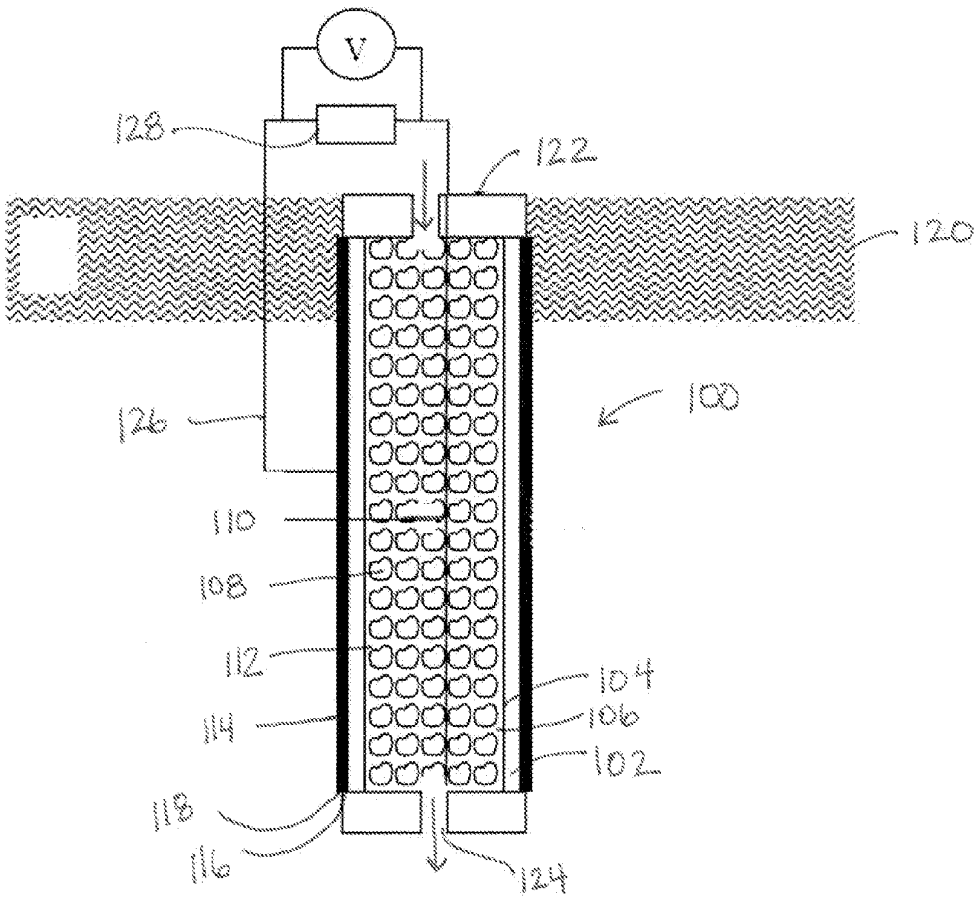
(51) **Int. Cl.**

H01M 8/16	(2006.01)
H01M 4/92	(2006.01)
H01M 4/96	(2006.01)

(52) **U.S. Cl.** **429/2**; 429/400

(57) **ABSTRACT**

A microbial fuel cell (MFC) includes a cation exchange membrane defining an anode chamber, an anode positioned in the anode chamber, and a cathode in contact with an exterior of the cation exchange membrane. A restrictor in contact with the cation exchange membrane defines an opening through which water flows into or out of the anode chamber. The MFC includes bacteria in the anode chamber that oxidize organic compounds in the water while oxygen is reduced at the cathode, such that electricity is generated in the absence of an external power source. In an example, the MFC is coupled to a buoy and provides electricity to an electrically powered device also coupled to the buoy, thereby providing a low-maintenance source of power in remote locations. The electrically powered device may be, for example, a light or a sensor.



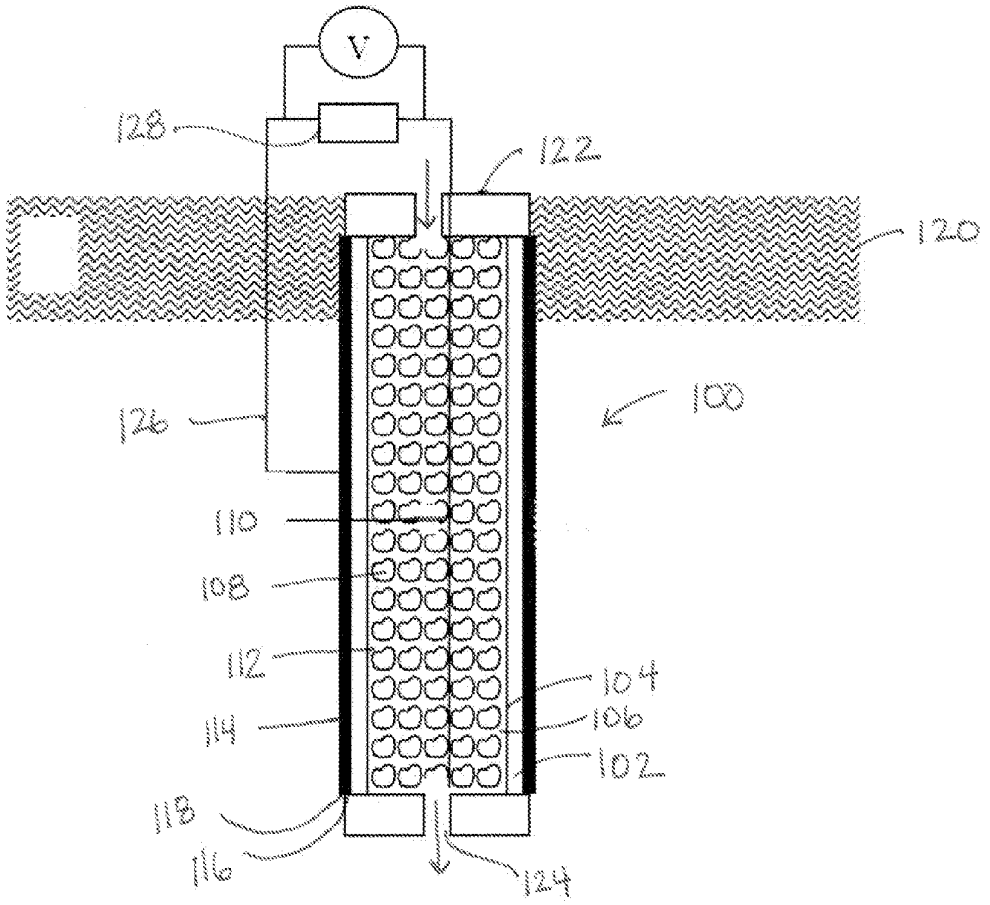

V
128
122
120
126
100
110
108
112
104
106
114
102
118
116
124

FIG. 1A

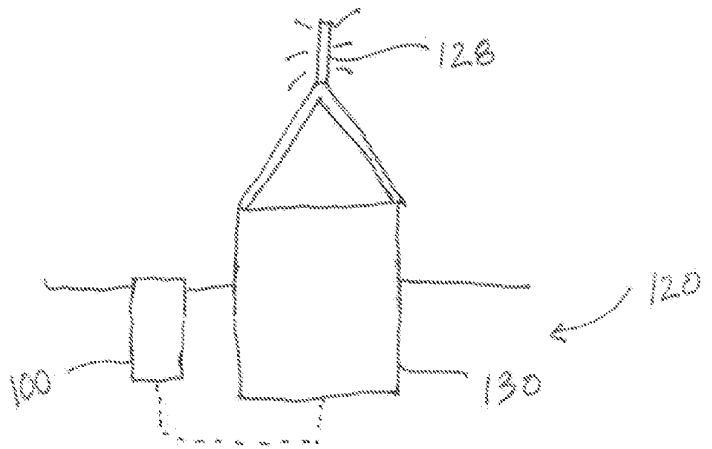

128
120
100
130

FIG. 1B

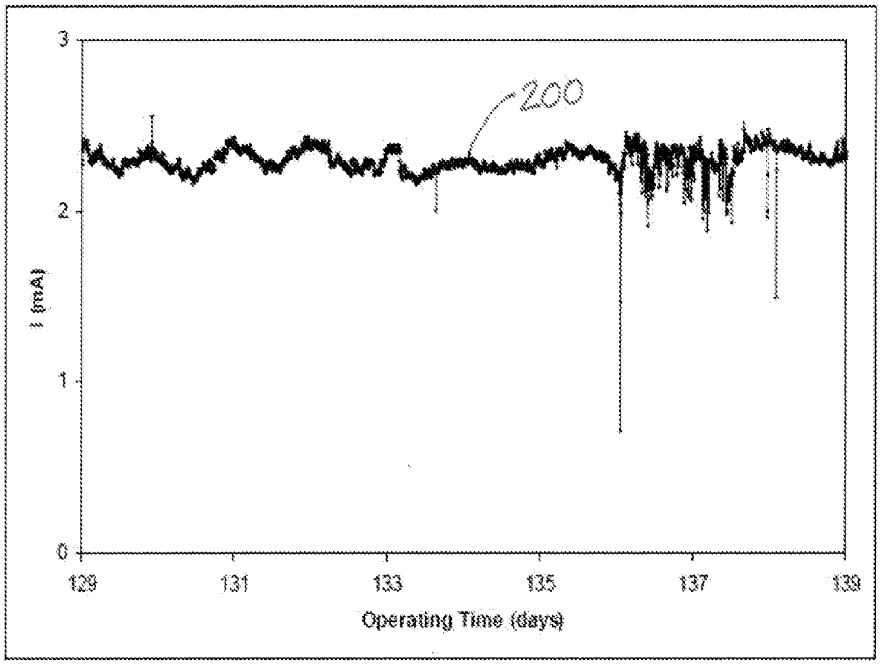

200
I (mA)
Operating Time (days)
0
1
2
3
129
131
133
135
137
139

FIG. 2

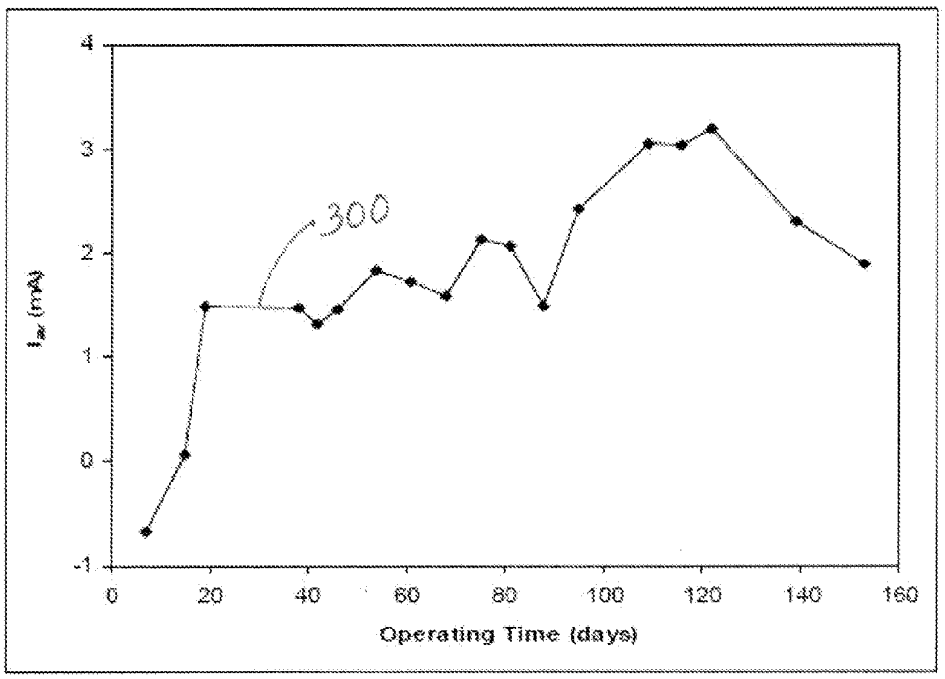

300
I_{sc} (mA)
Operating Time (days)
-1
0
1
2
3
4
0
20
40
60
80
100
120
140
160

FIG. 3

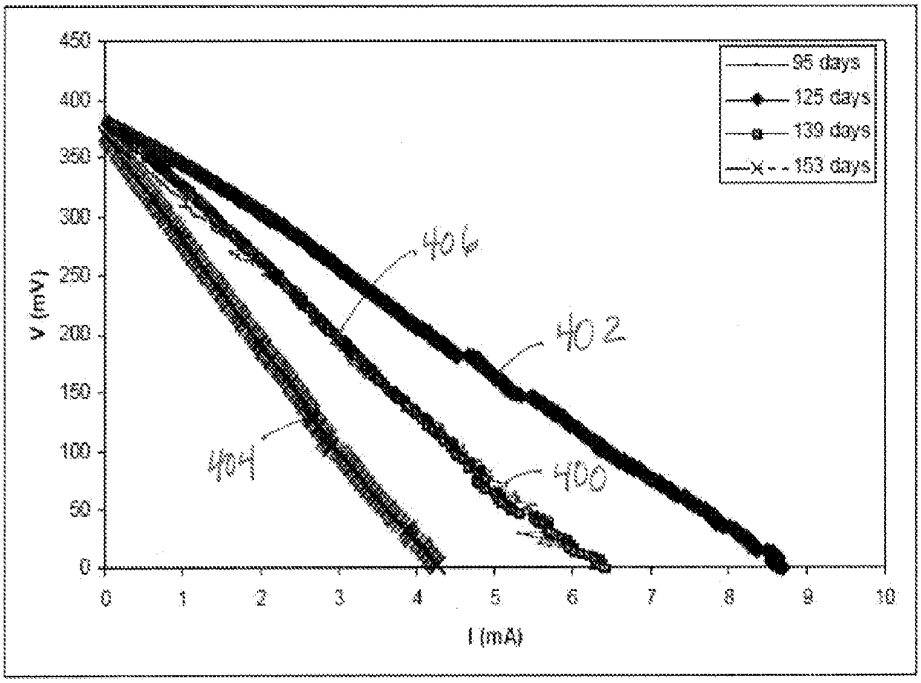

95 days
125 days
139 days
153 days
406
402
404
400
V (mV)
I (mA)

FIG. 4

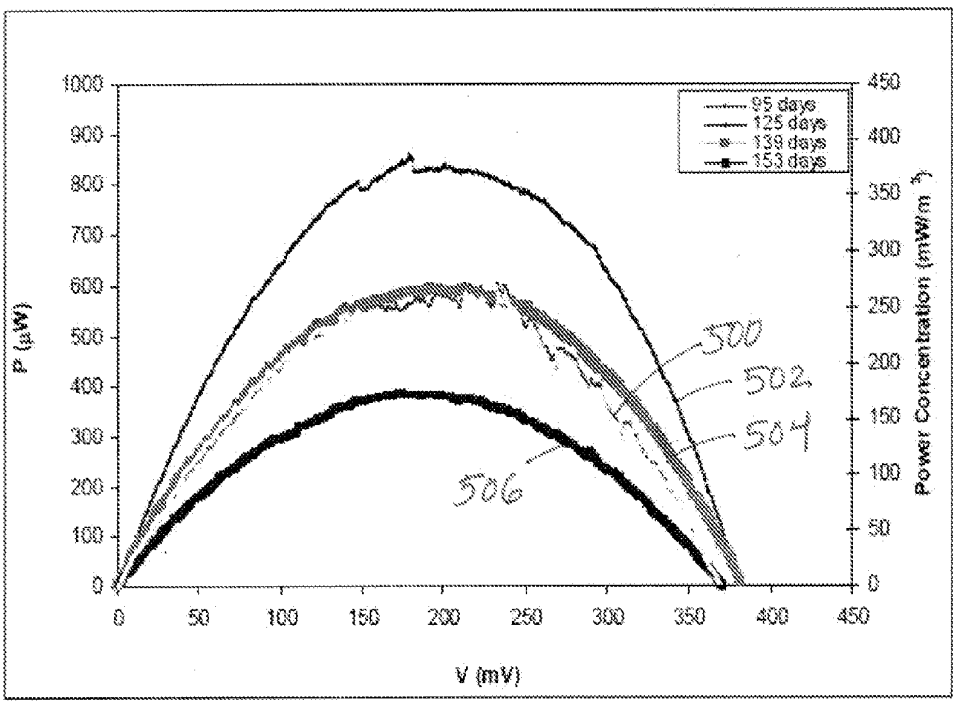

95 days
125 days
139 days
153 days
500
502
504
506
P (µW)
Power Concentration (mW/m²)
V (mV)

FIG. 5

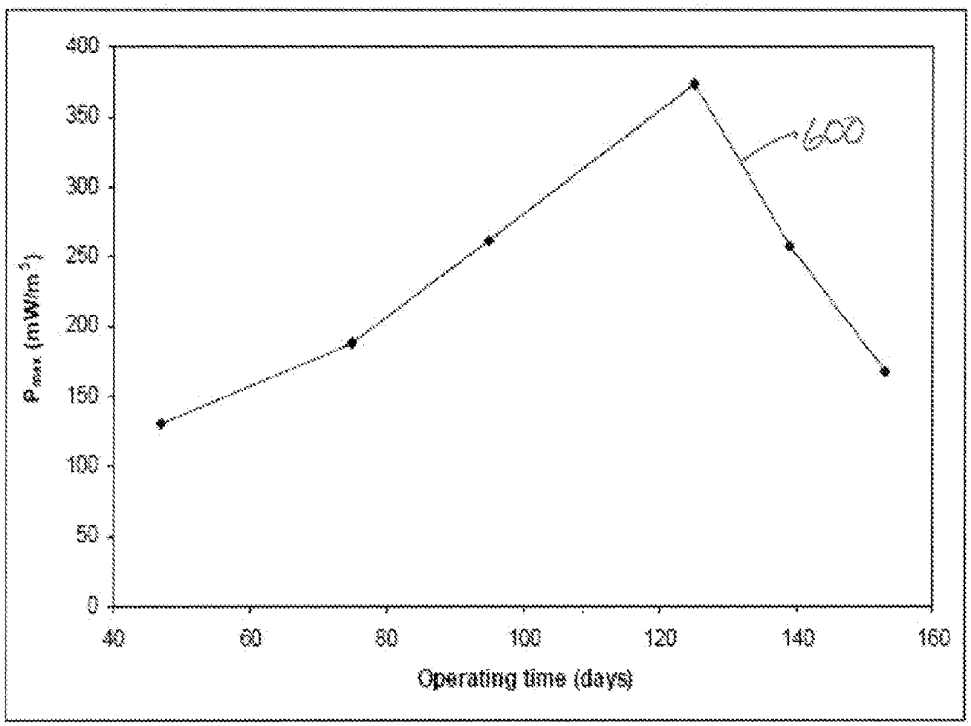

600
P_{max} (mW/m^2)
400
350
300
250
200
150
100
50
0
40
60
80
100
120
140
160
Operating time (days)

FIG. 6

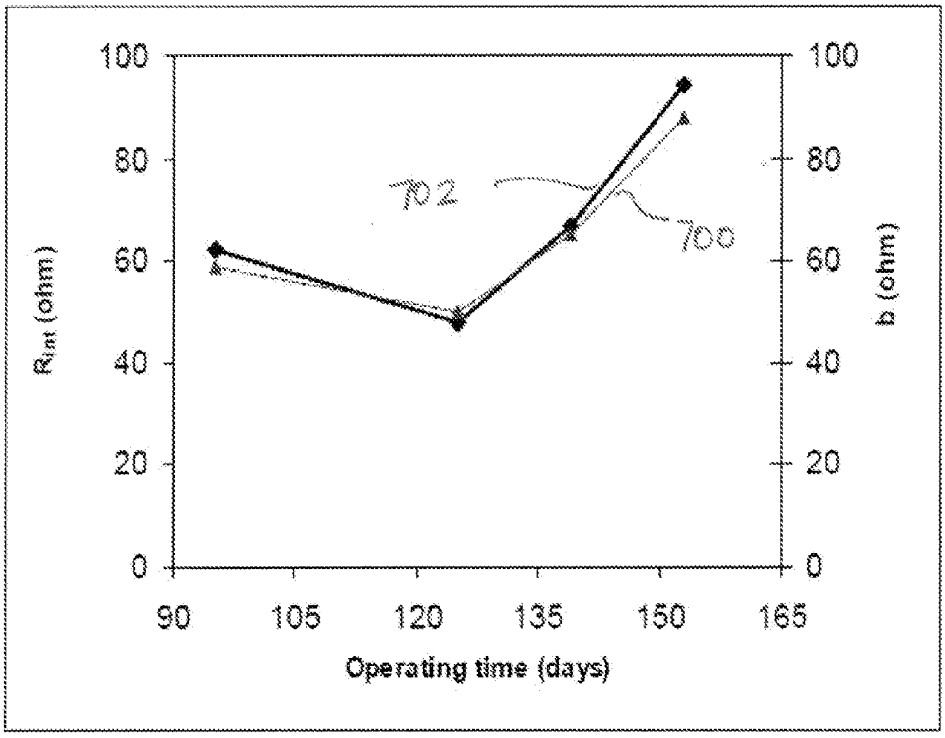

702
700
R_{int} (ohm)
b (ohm)
100
80
60
40
20
0
90
105
120
135
150
165
Operating time (days)

FIG. 7

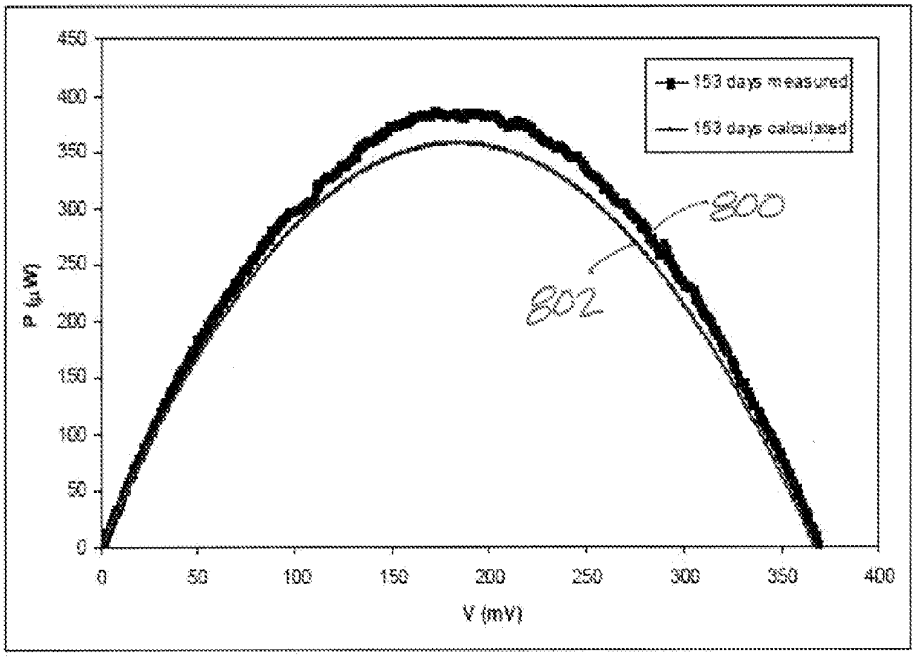

153 days measured
153 days calculated
800
802
P (μW)
V (mV)
0
50
100
150
200
250
300
350
400
450

FIG. 8

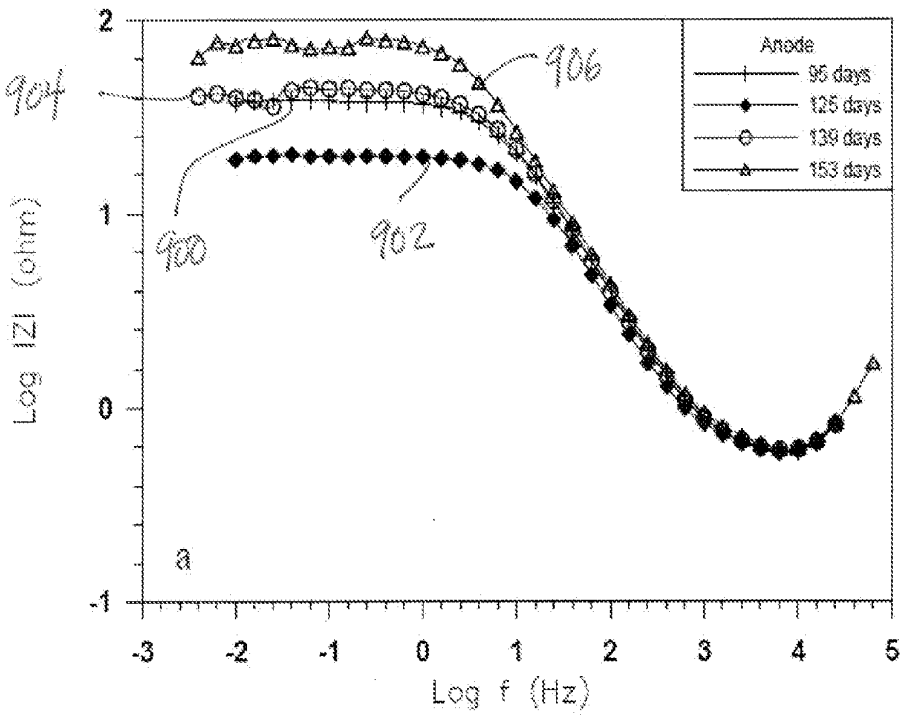

Anode
95 days
125 days
139 days
153 days
904
906
900
902
a
Log |Z| (ohm)
Log f (Hz)
2
1
0
-1
-3
-2
-1
0
1
2
3
4
5

FIG. 9

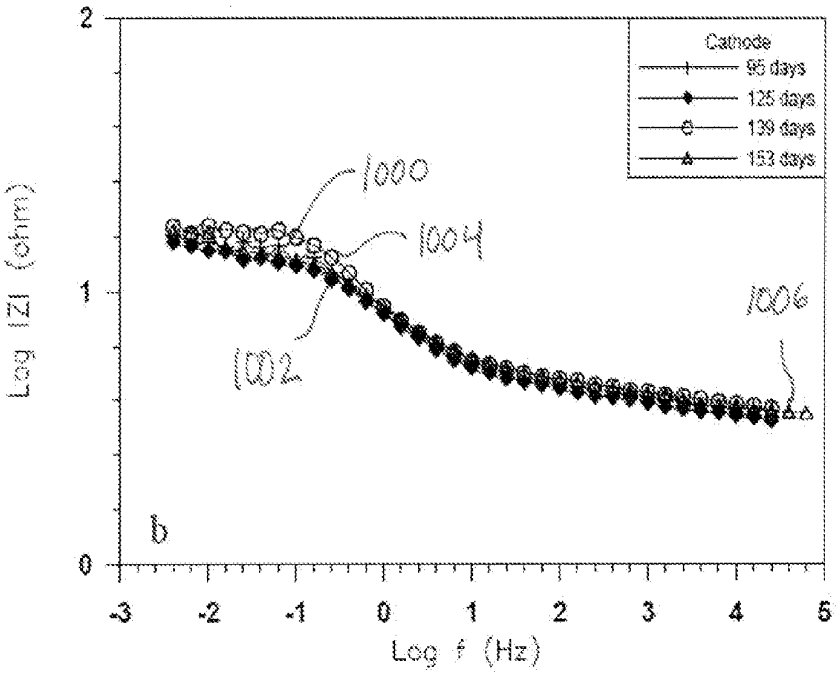

Cathode
95 days
125 days
139 days
153 days
1000
1004
1006
1002
b
Log |Z| (ohm)
Log f (Hz)
2
1
0
-3
-2
-1
0
1
2
3
4
5

FIG. 10

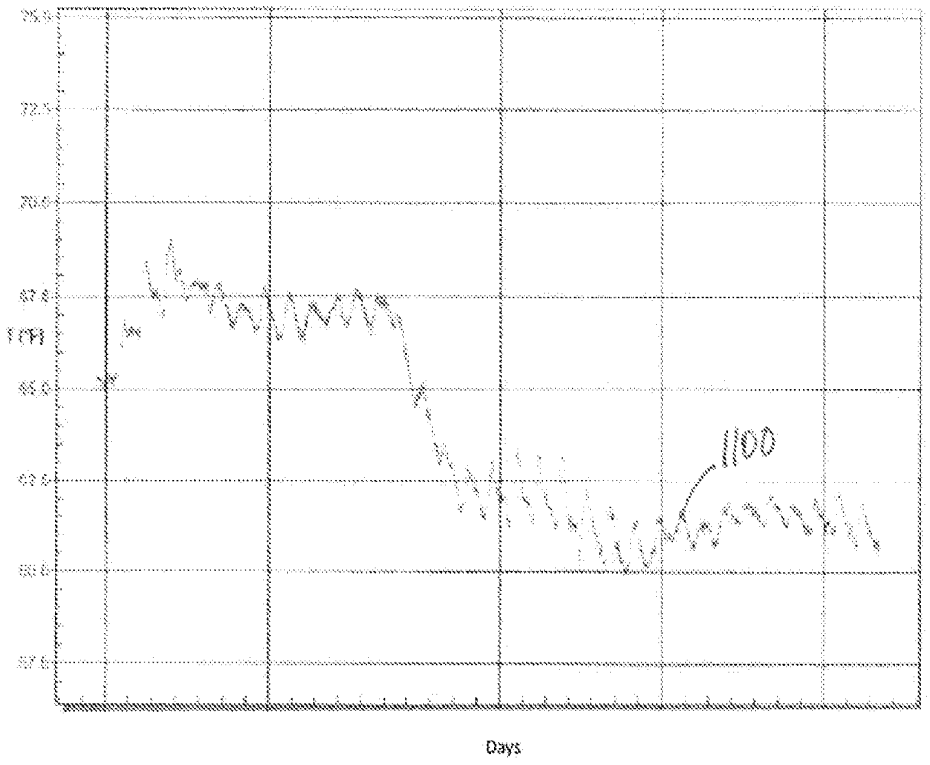

1100
Days

FIG. 11

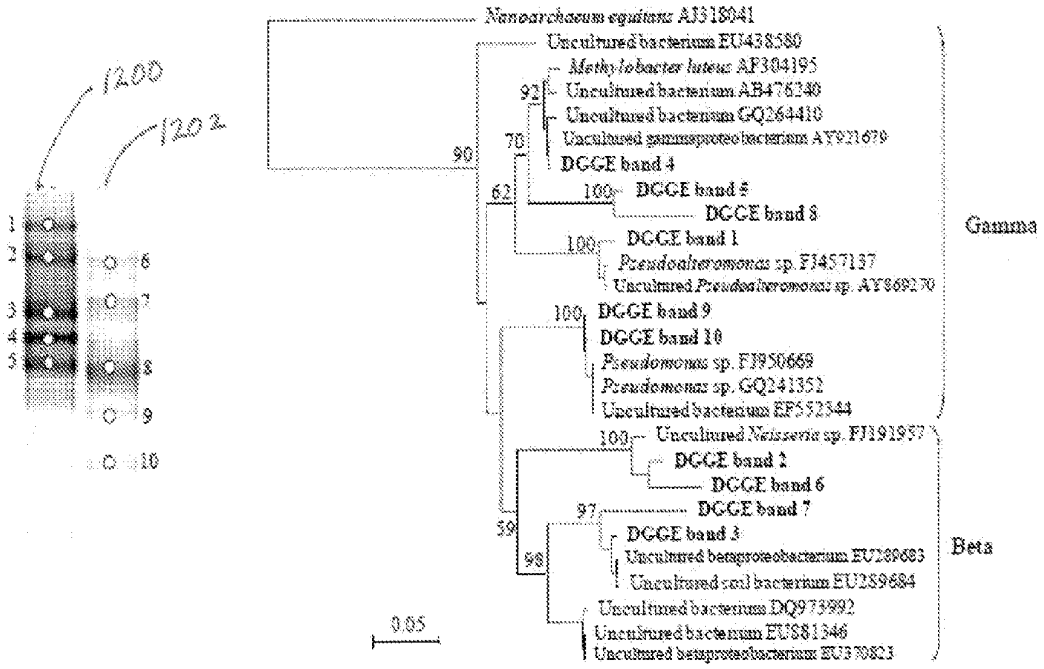


FIG. 12A

FIG. 12B

FLOATING MICROBIAL FUEL CELLS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Application Ser. No. 61/389,104, filed on Oct. 1, 2010, which is incorporated by reference herein.

TECHNICAL FIELD

[0002] This invention relates to floating microbial fuel cells.

BACKGROUND

[0003] Electrical energy can be harvested using sediment microbial fuel cells (SMFCs) that include an anode embedded in marine or river sediment and a cathode suspended in the aerobic water column above the anode. Bacteria inhabiting the sediment oxidize organic compounds and supply electrons to the anode while oxygen is reduced at the cathode. Among the different electrochemically active bacteria, *Desulfuromonace* spp. have been shown to be rich in marine sediments, while *Geobacter* spp. seem to predominate in freshwater sediments.

[0004] Electric power is typically provided to remote sensors or other electronic devices near large bodies of water via batteries. In some cases, the cost to replace the batteries may exceed the cost of the batteries themselves. SMFCs have been studied and developed to operate low-power consuming electronic devices installed in marine and river environments. While SMFCs may provide some advantages over current technologies, such as batteries, because of low cost and less frequent maintenance, the cathode is generally deployed close to the water surface to ensure sufficient oxygen supply, and the maximum distance between the anode and the cathode can be limited due at least in part to increased installation difficulties and ohmic drop. Thus, SMFCs may not be suitable in deep water at remote locations.

SUMMARY

[0005] In a first general aspect, a microbial fuel cell includes a cation exchange membrane defining an anode chamber, an anode positioned in the anode chamber, and a cathode in contact with an exterior of the cation exchange membrane. A restrictor in contact with the cation exchange membrane and defines an opening through which water flows into or out of the anode chamber.

[0006] In a second general aspect, an apparatus includes a buoy coupled to a microbial fuel cell as described by the first general aspect. In some cases, the apparatus includes an electrically powered device, and the microbial fuel cell is electrically coupled to the electrically powered device such that the microbial fuel cell provides electricity to the electrically powered device.

[0007] A third general aspect includes positioning a buoy comprising an electrically powered device and a microbial fuel cell in a body of water, and powering the electrically powered device with electricity generated by the microbial fuel cell.

[0008] Implementations of the above aspects may independently include one or more of the following features. For example, in some cases, the microbial fuel cell is cylindrical in shape. The cation exchange membrane can be tubular. The anode chamber defines a volume of at least 1 L, at least 2 L, at least 5 L, or at least 10 L. The anode may include carbon, such as granular carbon. The granular carbon may have a size in the range of 3 mm to 10 mm. In some cases, a size of the granular carbon is on the order of microns (e.g., 1 μm to 1000 μm). The size of the granular carbon can be selected to increase a surface-to-volume ratio of the anode while maintaining adequate mass transfer using the packed bed electrode principle. The anode may also include a conductive current collector made, for example, of titanium. The anode chamber includes bacteria (e.g., a mixture of aerobic and anaerobic bacteria) for oxidizing organic compounds.

[0009] The cathode of the microbial fuel cell includes a conductive material and a catalyst to facilitate reduction of oxygen at the cathode. In an example, the catalyst includes platinum. The conductive material and the catalyst are supported by an exterior surface of the cation exchange membrane, and an interior surface of the cation exchange membrane defines the anode chamber. In some cases, the catalyst is supported by the exterior surface of the cation exchange membrane, and the conductive material forms a layer on the catalyst. An additional layer of catalyst may be formed on the conductive material. The conductive material may include, for example, carbon fibers. In some cases, the carbon fibers have a metal coating.

[0010] In some implementations, the microbial fuel cell includes a second restrictor in contact with the cation exchange membrane, the second restrictor defining a second opening through which water flows into or out of the anode chamber.

[0011] The microbial fuel cell is operable to generate electricity in the absence of an external power source. The electrically powered device may be, for example, a light or a sensor. Electricity generated by the microbial fuel cell is used to power the electrically powered device.

[0012] The microbial fuel cell is a low-cost, low-maintenance source of continuous electricity for electrically powered devices in remote locations and/or deep water settings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. **1**A is a schematic diagram of an example of a floating microbial fuel cell (FMFC).

[0014] FIG. **1**B depicts a FMFC coupled to a buoy.

[0015] FIG. **2** is a plot of current vs. time for a FMFC from day **129** to day **139** of operation.

[0016] FIG. **3** is a plot of average current vs. operating time for a FMFC.

[0017] FIG. **4** shows cell voltage-current curves for different operating times of a FMFC.

[0018] FIG. **5** shows power and power concentration-cell voltage curves for different operating times of a FMFC.

[0019] FIG. **6** is a plot of P_{max} vs. operating time for a FMFC.

[0020] FIG. **7** shows internal resistance and slope of the voltage-current curves shown in FIG. **4** as a function of operating time.

[0021] FIG. **8** shows a comparison of measured and calculated power-cell voltage curves for a FMFC with an operating time of 153 days.

[0022] FIG. **9** shows Bode plots for the anode of a FMFC for different operating times.

[0023] FIG. **10** shows Bode plots for the cathode of a FMFC for different operating times.

[0024] FIG. **11** shows a digital recording of seawater temperature at a FMFC test location.

[0025] FIG. **12**A shows denaturing gradient gel electrophoresis (DGGE) fingerprints of bacterial communities (anode and mixed innoculums).

[0026] FIG. **12**B shows a phylogenetic analysis of DGGE band sequences shown in FIG. **12**A.

DETAILED DESCRIPTION

[0027] Referring to FIG. **1**A, floating microbial fuel cell (FMFC) **100** includes cation exchange membrane **102**. Cation exchange membrane **102** defines anode chamber **104**. A shape of FMFC **100** or a shape of cation exchange membrane **102** may be, for example, cylindrical (e.g., tubular), spherical, cubic, or any other shape configured to define anode chamber **104**. A volume of anode chamber **104** may be at least 1 L, at least 2 L, at least 5 L, or at least 10 L. In some cases, FMFC **100** includes more than one anode chamber (e.g., 2, 4, 6, 8, 10, or more).

[0028] Anode **106** in anode chamber **104** includes anode material **108** and current collector(s) **110**. Anode material **108** includes, for example, granular carbon. A size of the granular carbon may be in a range of 3 mm to 10 mm, or on micron scale (e.g., 1 μm to 1000 μm). The power output of FMFC can be increased by increasing the surface-to-volume ratio of the anode while maintaining adequate mass transfer using the packed bed electrode principle.

[0029] Current collector(s) **110** may include conductive members, such as wires or rods formed from titanium, gold, or the like. The anode chamber may be inoculated with bacteria **112**. Bacteria **112** may be provided to anode chamber **104** in the form of anaerobic sludge, aerobic sludge, or a mixture thereof. The sludge may be obtained from a wastewater treatment plant or may include sediment from a body of water, such as a river, lake or ocean. The sludge includes a mixture of electrochemically active aerobic and anaerobic bacteria that oxidize organic compounds in the water inside anode chamber **104** and supply electrons to the anode. Examples of suitable bacteria include Beta and Gammaproteobacteria.

[0030] Cathode **114** is supported by cation exchange membrane **102**. Cathode **114** includes catalyst **116** and conductive material **118**. The catalyst facilitates reduction of oxygen at the cathode. In some cases, catalyst **116** and conductive material **118** are applied in layers to cathode **114** (e.g., a first layer of catalyst, a conductive material, a second layer of catalyst). In other cases, a mixture of catalyst **116** and conductive material **118** is applied to the exterior surface of cation exchange membrane **102**. Catalyst **116** may include, for example, platinum or other catalysts used to facilitate reduction of oxygen in the water. Conductive material **118** may include carbon fibers, carbon nanotubes, carbon nanowires, carbon nanoparticles, or the like. In some cases, conductive material **118** is coated with a metal, such as nickel or the like.

[0031] In some cases, FMFC **100** has an associated buoyancy that causes FMFC **100** to float in water **120**. Buoyancy may be associated with anode chamber **104**, for example, in a gas-filled compartment. In certain cases, buoyancy is provided by a ballast system or buoy coupled to FMFC **100**. In an example, FMFC may be installed in a buoy flowing on water **120**. Water **120** may be part of a lake, river or ocean. FMFC **100** includes one or more restrictors **122**. Restrictor(s) **122** may be in contact with cation exchange membrane **102**. Each restrictor **122** defines one or more openings **124** through which water **120** flows into or out of anode chamber. The arrows in FIG. **1**A indicate a flow of water into anode chamber **104** through a first opening **124** and out of the anode chamber through a second opening. The area of openings **124** may be selected to allow sufficient circulation of water through the anode chamber while inhibiting excessive oxygen flux into the anode chamber.

[0032] Anode **106** is electrically coupled to cathode **114** via conductor **126**. FMFC **100** may be used to provide electricity to low-power consuming electronic devices at remote locations (e.g., deep marine locations). In some cases, FMFC **100** is electrically coupled to electrically powered device **128**. Electrically powered device **128** may be, for example, a component of a buoy. The component may be, for example, a light or a sensor. FMFC **100** generates electricity in the absence of an external power source when placed in body of water **120**. The generated electricity may be continuous, and may be used to power electrically powered device **128**. Thus, FMFC **100** may be used as low-cost, low-maintenance alternative to batteries proximate bodies of water.

[0033] FIG. **1**B shows FMFC **100** coupled to buoy **130** in water **120**. FMFC **100** can be secured to buoy **130**. In some cases, FMFC **100** is electrically coupled to electrically powered device **128** and provides a low-cost, low maintenance, continuous source of electricity for the electrically powered device. FMFC **100** can be advantageously used in remote locations and/or deep water settings, with all components of the FMFC located together at and accessible from the surface of the water. Other configurations are also possible, including integrating FMFC **100** with buoy **130** at the time of manufacture.

EXAMPLES

[0034] A single-chamber tubular FMFC was designed, and its performance was evaluated for 153 days using different electrochemical techniques. The FMFC was allowed to float at the ocean surface hanging from a cable attached to a dock at Long Beach Harbor, Calif. Over the period of operation of the FMFC, the cell current and the power output gradually increased to maximum values at 125 days and then decreased. A linear relationship between cell voltage (V) and current (I) was observed. The slopes of the V-I curves were close to the experimental values of the internal resistance (R_{int}) that were obtained from the power (P)-V curves or from analysis of the impedance data. The maximum current (I_{max}), the P-V curves and maximum power output (P_{max}) were calculated based on the experimental values of the open-circuit cell voltage (V_o) and R_{int}. Impedance spectra were collected at the open-circuit potentials of the anode and cathode. The polarization resistance of the anode (R_{ap}) changed with operating time, reaching a minimum value at 125 days, while the polarization resistance of the cathode (R_{cp}) was relatively constant and smaller than R_{ap}. Results suggest that electricity was constantly produced by the FMFC, and that the observed changes of R_{int} and P_{max} with exposure time were due at least in part to the changes of R_{ap}. PCR-DGGE analysis of microbial communities showed the development of unique bacterial species on the anode during operation.

[0035] The FMFC described in this example was constructed using a tube made of cation exchange membrane (Ultrex CMI7000, Membranes International, USA). The tube had a diameter of 9 cm and a length of 70 cm with a total anode volume of 4.5 L. The top and bottom of the tube were covered with rubber stoppers. Each rubber stopper had a small hole with a diameter of 8 mm to allow circulation of ocean water through the FMFC while inhibiting excessive

oxygen flux into the anode chamber. Granular graphite (diameter about 10 mm, Carbon Activated Corp, Compton, Calif., USA) was used to fill the tube and to function as the anode, resulting in an anode liquid volume of 2.3 L. Three titanium wires were inserted into the granular graphite as current collectors.

[0036] Before being deployed in the ocean, the FMFC was operated in the laboratory to examine its electricity generation from organic compounds. It was fed continuously with a solution containing: $NaC_2H_3O_2.3H_2O$ (3 g/L); yeast extract (0.2 g/L); NH_4Cl (1 g/L); $MgSO_4$ (0.25 g/L); NaCl (0.5 g/L); $CaCl_2$ (15 mg/L); trace solution (1 mL/L) (He et al., Spectroscopy. Environ. Sci. Technol., 40, 5212-5217, which is incorporated by reference herein.), and phosphate buffered nutrient medium (100 mL/L) containing NaH_2PO_4 (50 g/L) and Na_2HPO_4 (107 g/L). Forty mL of a mixture of anaerobic and aerobic sludge (50/50) that was collected from a wastewater treatment plant (Joint Water Pollution Plant, CA) were injected into the anode chamber as inoculum.

[0037] The cathode included Ni-coated carbon fibers (TenaX®-J, Toho Tenax Co., Ltd., grade HTS 40, Irvine, Calif., USA) and two catalyst layers. To make a catalyst layer, powder of Pt/C (10% Pt, Etek, Somerset, N.J., USA) was mixed with tap water to form a paste that was applied to the outer surface of the membrane tube using a brush. This layer was then covered by carbon fibers. The second catalyst layer (same composition as the first catalyst layer, but mixed with a Nafion solution) was applied to the outside of the carbon fibers. The catalysts layers were air dried for 48 hours at room temperature before operation.

[0038] Before deployment of the FMFC, the feeding had been stopped for a few days to allow the voltage to drop to very low levels (<10 mV). In addition, to facilitate the transport of the FMFC from the lab to the test site, the solution inside the FMFC was decanted. That also reduced the chance of electricity generation from the remaining organics (if any) during the deployment in the sea. After the laboratory examination and operation, the tubular MFC was installed hanging from a cable that was attached to a dock at the seawater surface at Long Beach Harbor, Calif. for 153 days during which time electrochemical measurements were performed.

[0039] The voltage across an external resistor (R_{ext}) of 100 ohm was recorded every 4 minutes for 153 days using a data logging multimeter. Cell voltage (V)-current curves (I) were recorded by applying a potentiodynamic scan at a scan rate of 0.2 mV/s from the open-circuit cell voltage (V_o) to the short-circuit cell voltage (V_{sc}). During this measurement, the anode of the FMFC was connected to the working electrode lead and the cathode was connected to the counter and reference electrode leads of the potentiostat. Impedance spectra were collected at the open-circuit potentials (OCP) of the anode and cathode. An AC voltage signal of 10 mV was applied in a frequency range from 100 kHz to 5 mHz. A saturated calomel electrode (SCE) placed in the seawater next to the FMFC was used as the reference electrode. Electrochemical impedance spectroscopy (EIS) measurements were conducted by first recording the impedance spectrum of the anode with the cathode acting as counter electrode (CE) followed by recording of the spectra for the cathode with the anode serving as CE. These electrochemical measurements were performed in the seawater at Long Beach Harbor, Calif. using a Gamry reference 600 potentiostat (Garmry Instruments, Warminster, Pa., USA).

[0040] Genomic DNA was extracted using an ULTRACLEAN™ Soil DNA kit (MO BIO Laboratories, Carlsbad, Calif.) from mixed inoculums and graphite beads in the anode electrode following the manufacturer's instructions. Polymerase chain reaction (PCR) and denaturing gradient gel electrophoresis (DGGE) analyses were performed as previously described (He et al., Environ. Sci. Technol., 43 (2009): 3391-3397 and Kan et al., Aquat. Microb. Ecol., 42 (2006): 7-18, both of which are incorporated by reference herein) by using the primers **1070***f* and **1392***r* (Ferris et al., Appl. Environ. Microbiol., 62 (1996): 340-346, which is incorporated by reference herein).

[0041] Representative bands excised from DGGE gel were re-amplified and PCR products were purified by ExoSAP-IT (USB, Cleveland, Ohio) and sequenced with primer **1070***f* by using Bigdye terminator chemistry by ABI PRISM3100 Genetic Analyzer (Applied Biosystems, Foster City, Calif.). All sequences were compared with GenBank database using BLAST, and the closest matched sequences were obtained and included in the phylogeny reconstruction (He et al., 2009 and Kan et al., 2006). *Nanoarchaeum equitans* was used as an outgroup. Bootstrap values were calculated based on 1000 resampling datasets. For clarity, only bootstrap values relevant to the interpretation of groupings were shown. The scale bar indicates the number of substitutions per site. DGGE band sequences have been deposited in the GenBank database under accession numbers GU938704-GU938713.

[0042] The performance of the FMFC was investigated using different electrochemical techniques. An example of the recorded current-time curves **200** is shown in FIG. **2** for the operating period between 129 and 139 days. The cell current had an average value of 2.35 mA and remained relatively constant during these ten days of operation. FIG. **3** shows plot **300** of average cell currents as a function of operation time. Each current point plot **300** was obtained as the average value for an operating time of 3 to 10 days. The current increased to 1.5 mA during the first 20 days of operation, indicating a transformation of lab freshwater MFC to a seawater MFC. During next 70 days, the current varied between 1.5 and 2.2 mA. Another increase of the current to 3.3 mA occurred until 125 days followed by a decrease of the current. At the end of exposure the current had decreased to 1.9 mA.

[0043] The V-I and P-V curves obtained at four different operating periods are shown in FIG. **4** and FIG. **5**, respectively. The open-circuit cell voltage (V_o) for the entire operating period was about 380 mV. This low V_o may be due to the presence of dissolved oxygen in the anode compartment as indicated by a high anode potential (between −54 to −15 mV vs. SCE). FIG. **4** shows plots **400**, **402**, **404**, and **406** corresponding to operating times of 95 days, 125 days, 139 days, and 153 days, respectively. The highest short-circuit current of 8.7 mA occurred at 125 days and the lowest of 4.2 mA was at 153 days of operation.

[0044] FIG. **5** shows the values of the power and the power concentration $P^*=P/V_a$ (where V_a is the anode liquid volume), which were calculated from the measured V-I curves shown in FIG. **4** as a function of the cell voltage. Plots **500**, **502**, **504**, and **506** correspond to an operating time of 95 days, 125 days, 139 days, and 153 days, respectively.

[0045] Plot **600** in FIG. **6** shows that P_{max} increased continuously from 46 days to 125 days of operation, and then decreased until the end of exposure. Similar to the observed current trend, the maximum P* increased from 260 mW/m^3 at

95 days to 390 mW/m^3 at 125 days at a cell voltage of around 200 mV and then decreased to 156 mW/m^3 after 153 days.

[0046] The V-I curves shown in FIG. **4** can be expressed as:

$$V_{cell}=V_o-bI, \quad (1)$$

where V_{cell} is the cell voltage, V_o is the open-circuit voltage, I is the current and b is the slope of the V-I curves. At the cell voltage V_{max}, where the maximum power output P_{max} occurs, $R_{int}=R_{ext}$, where R_{int} is the internal resistance of the MFC and R_{ext} is the external resistor that is placed between the anode and the cathode to obtain V_{max} (Manohar et al., Bioelectrochemistry, 72 (2008): 149-154, which is incorporated herein by reference). R_{int} can be calculated as:

$$R_{int}=V^2_{max}/P_{max}. \quad (2)$$

[0047] FIG. **7** shows that the slopes that were obtained from the V-I curves in FIG. **4** (plot **700**) are in good agreement with R_{int} (plot **702**). Therefore, Eq. 1 becomes:

$$V_{cell}=V_o-IR_{int}. \quad (3)$$

For $V_{cell}=0$, Eq. 3 can be expressed as:

$$I_{max}=V_o/R_{int}, \quad (4)$$

where I_{max} is the maximum current produced by the MFC. The V-I curves can be calculated as:

$$P=V_{cell}I=(V_oV_{cell}-V^2_{cell})/R_{int}. \quad (5)$$

P_{max} can be obtained based on Eq. 2:

$$P_{max}=V^2_{max}/R_{int}. \quad (6)$$

$$\text{From } dP/dV=(V_o-2V_{cell})/R_{int}=0, \quad (7)$$

$$\text{one can obtain } V_{max}=0.5V_o. \quad (8)$$

$$\text{Therefore } P_{max}=V^2_o/4R_{int}. \quad (9)$$

[0048] Table 1 gives a comparison of the measured and calculated P_{max} values for different operating times. Good agreement between the measured and the calculated P_{max} values was observed. Plots **800** and **802** in FIG. **8** show a comparison of measured and calculated P-V curves (Eq. 5), respectively, for an operating time of 153 days. Good agreement was observed between the measured P-V curve and the P-V curve calculated using Eq. 5. These results show that for linear V-I curves, the maximum current I_{max} produced by the MFC, the P-V curves and P_{max} can be calculated using the experimental values of V_o and R_{int}.

TABLE 1

Comparison of measured and calculated maximum power output (Eq. 6).

Operating Time	P_{max} (μW)	
(days)	Measured	Calculated
95	582	542
125	829	744
139	591	547
153	384	358

[0049] The impedance spectra for the anode shown in plots **900**, **902**, **904**, and **906** of FIG. **9** for 95 days, 125 days, 139 days, and 153 days, respectively, were analyzed using the BASICZ module of the ANALEIS software (Mansfeld et al., ASTM STP, 1188 (1993): 37-53, which is incorporated by reference herein). The equivalent circuit (EC) used contains an ohmic resistance (R_Ω) which is in series with the polarization resistance (R_p) which is in parallel with a capacitance (C). The fit parameters of the anode and cathode obtained for four different operating times are listed in Table 2 and Table 3, respectively. The capacitance (C_a) of the anode did not change significantly during the entire operating period. However, the polarization resistance of anode (R_{ap}) decreased to 20Ω during the first 125 days of exposure and increased to 79Ω after 153 days (FIG. **9** and Table 2), similar to the observed variations of current and power (FIG. **4** and FIG. **5**), suggesting that electricity generation by the FMFC was mainly determined by the anode performance.

TABLE 2

Fit parameters of EIS data and OCP for the anode of the FMFC.

Operating time (days)	95	125	139	153
R_Ω (ohm)	0.52	0.58	0.57	0.60
R_{ap} (ohm)	40	20	44	79
C_a (μF)	880	970	840	680
OCP (mV)	−46	−54	−36	−15

[0050] The impedance spectra for the cathode shown in plots **1000**, **1002**, **1004**, and **1006** of FIG. **10** for 95 days, 125 days, 139 days, and 153 days, respectively, showed little change with operating time. The fit parameters of the impedance spectra and the OCPs for the cathode are shown in Table 3. The very low impedance is considered to be due to the large surface area of carbon fibers of the cathode. The OCP of the anode decreased from −46 mV at 95 days to −54 mV at 125 days and then increased to its highest value of −15 mV after 153 days, while the open-circuit potentials (OCP) of cathode remained more or less constant between 324 mV and 352 mV during the operating time.

TABLE 3

Fit parameters of EIS data and OCP for the cathode of the FMFC.

Operating time (days)	95	125	139	153
R_Ω (ohm)	3.38	3.15	3.48	3.33
R_{cp} (ohm)	15	16	21	17
C_c (mF)	200	650	390	420
OCP (mV)	338	324	347	352

[0051] R_{int} has been defined as (Manohar et al., 2008):

$$R_{int}=R_{ap}+R_{cp}+R_\Omega, \quad (10)$$

where RΩ contains the ohmic losses such as the solution resistance between the anode and the cathode, the membrane resistance and the electrical resistance of the electrodes, leads, etc. The ohmic contribution to the internal resistance was very small (Tables 2 and 3). The R_{int} values determined from Tables 2 and 3 using Eq. 10 are in very good agreement with the slopes of the V-I curves in FIG. **4** and the R_{int} values that were calculated using Eq. 2. R_{cp} did not change significantly during the entire operating period. However, R_{ap} changed with operating time reaching a minimum value at 125 days. These results suggest that the observed changes of R_{int} were mainly due to the changes of R_{ap}. Since P_{max} depends on the values of R_{int}, it can be concluded that the observed changes of P_{max} with operating time were due to the changes of R_{ap}. The power output could be increased by lowering R_{ap} which could be achieved by reducing the size of the carbon granules used to increase the surface-to-volume

ratio for the anode, while maintaining adequate mass transfer using the packed bed electrode principle (Manohar et al., Electrochim. Acta, 54 (2009): 1664-1670, which is incorporated herein by reference).

[0052] The digital records of the seawater temperature shown in plot **1100** of FIG. **11** were collected at the FMFC test location for the operating time of 120 days to 153 days. The temperature of the seawater decreased from 132 days to 153 days of operation. As shown in FIG. **9**, R_{ap} increased from 135 days until the end of operation (153 days). The decreased temperature could possibly reduce the anode microbial activities and therefore increase R_{ap}. As a result, the current and the power showed a similar decrease variation from 139 days to 153 days (FIG. **4** and FIG. **5**). While changes of the seawater temperature likely has an effect on the measured I and P values, it should be noted that seawater temperature may not be the only factor that affects microbial processes.

[0053] DGGE results shown in FIG. **12**A indicate that bacterial populations occurring in the anode compartment (**1200**) were distinct compared to the bacterial populations in the inoculums (**1202**), suggesting that microbial population structures shifted during the FMFC operation.

[0054] Phylogenetic analysis shown in FIG. **12**B demonstrated that bacterial sequences obtained from both inocula and the anode belonged to Beta and Gammaproteobacteria. Band 1 (close to *Pseudoalteromonas* sp.) and band 4 (gammaproteobacterium) were unique to the anode community. Gammaproteobacteria have been detected in microbial fuel cell studies. For example, *Pseudoalteromonas* sp. (band 1 in this report) was also found in a marine sediment microbial fuel cell fed with cysteine (Logan et al., Water Res., 39, 942-952 (2005), which is incorporated by reference herein), suggesting that this group of bacteria may play a role in terms of exoelectron transport and/or power generation. In contrast, *Pseudomonas* spp. (band 9 and 10) were only present in inocula, but disappeared in enriched anodic communities. Bands 6 and 7 were clustered together with bands from anode (bands 2 and 3), but phylogenetic distance indicated that they are different from the phylotypes in anode (i.e., <95% similarity). Band 5 (from anode) and band 8 (from inocula) were closely related, but identified as uncharacterized gammaproteobacteria with unknown physiological capabilities. Nevertheless, enriched mixed bacterial communities may contribute to exoelectrogenic activities occurring in the FMFC.

[0055] In summary, electricity was produced from the FMFC over the 153 days of operation. The power gradually increased for the first 125 days and then decreased. The V-I curves obtained using a potentiodynamic scan at four different operating periods showed a linear relationship between V and I. For linear V-I curves I_{max} produced by the MFC, the P-V curves and P_{max} can be calculated based on the experimental values of V_o and R_{int}.

[0056] The polarization resistance of the cathode (R_{cp}) did not show significant changes during the entire operating time, while the polarization resistance of the anode (R_{ap}) decreased for the first 125 days and then increased until the end of operation. The ohmic contribution to R_{int} was small. The stable and low R_{cp} values suggest that the observed changes of R_{int} were mainly due to the changes of R_{ap}. These results suggest that the observed changes in power generation during the operating time are due to the changes of R_{ap}, which exhibited a similar trend as the variations of the cell current and power concentration.

[0057] The continuous electricity production during the long-term operation (more than 120 days) suggests that the FMFC was able to utilize organic compounds and nutrients from seawater for energy production. The cell current decrease observed at the end of exposure may be due at least in part to the decrease of the ocean temperature.

[0058] Molecular analyses (PCR-DGGE) revealed that distinct bacterial groups were developed and enriched in the anode compartment of the FMFC, suggesting these groups played roles in power generation and/or carbon source utilization.

[0059] A number of embodiments have been described. Nevertheless, it will be understood that various modifications may be made without departing from the spirit and scope of the disclosure. Accordingly, other embodiments are within the scope of the following claims.

What is claimed is:

1. A microbial fuel cell comprising:
a cation exchange membrane defining an anode chamber;
an anode positioned in the anode chamber;
a cathode in contact with an exterior of the cation exchange membrane; and
a restrictor in contact with the cation exchange membrane and defining an opening through which water flows into or out of the anode chamber

2. The microbial fuel cell of claim **1**, wherein the microbial fuel cell is cylindrical in shape.

3. The microbial fuel cell of claim **1**, wherein the cation exchange membrane is tubular.

4. The microbial fuel cell of claim **1**, wherein the anode chamber defines a volume of at least 1 L.

5. The microbial fuel cell of claim **1**, wherein the anode comprises carbon.

6. The microbial fuel cell of claim **5**, wherein the carbon comprises granular carbon.

7. The microbial fuel cell of claim **6**, wherein a size of the granular carbon is in a range between 3 mm and 10 mm.

8. The microbial fuel cell of claim **1**, wherein the anode comprises a conductive current collector.

9. The microbial fuel cell of claim **1**, wherein the cathode comprises a conductive material and a catalyst to facilitate reduction of oxygen at the cathode.

10. The microbial fuel cell of claim **9**, wherein the conductive material and the catalyst are supported by an exterior surface of the cation exchange membrane, and an interior surface of the cation exchange membrane defines the anode chamber.

11. The microbial fuel cell of claim **10**, wherein the catalyst is supported by the exterior surface of the cation exchange membrane, and the conductive material forms a layer on the catalyst.

12. The microbial fuel cell of claim **11**, further comprising additional catalyst forming a layer on the conductive material.

13. The microbial fuel cell of claim **9**, wherein the conductive material comprises carbon fibers.

14. The microbial fuel cell of claim **13**, wherein the conductive material comprises a metal coating supported by the carbon fibers.

15. The microbial fuel cell of claim **9**, wherein the catalyst comprises platinum.

16. The microbial fuel cell of claim **1**, further comprising a second restrictor in contact with the cation exchange mem-

brane, the second restrictor defining a second opening through which water flows into or out of the anode chamber.

17. The microbial fuel cell of claim **1**, wherein the microbial fuel cell is operable to generate electricity in the absence of an external power source.

18. The microbial fuel cell of claim **1**, wherein the anode chamber comprises bacteria for oxidizing organic compounds.

19. The microbial fuel cell of claim **1**, wherein the microbial fuel cell has an associated buoyancy that causes the microbial fuel cell to float.

20. An apparatus comprising:

a buoy; and

a microbial fuel cell coupled to the buoy, the microbial fuel cell comprising:

a cation exchange membrane defining an anode chamber;

an anode positioned in the anode chamber;

a cathode in contact with an exterior of the cation exchange membrane; and

a restrictor in contact with the cation exchange membrane and defining an opening through which water flows into or out of the anode chamber.

21. The apparatus of claim **20**, wherein the buoy comprises an electrically powered device, the microbial fuel cell is electrically coupled to the electrically powered device, and the microbial fuel provides electricity to the electrically powered device.

22. A method comprising:

positioning a buoy comprising an electrically powered device and a microbial fuel cell in a body of water; and

powering the electrically powered device with electricity generated by the microbial fuel cell.

* * * * *