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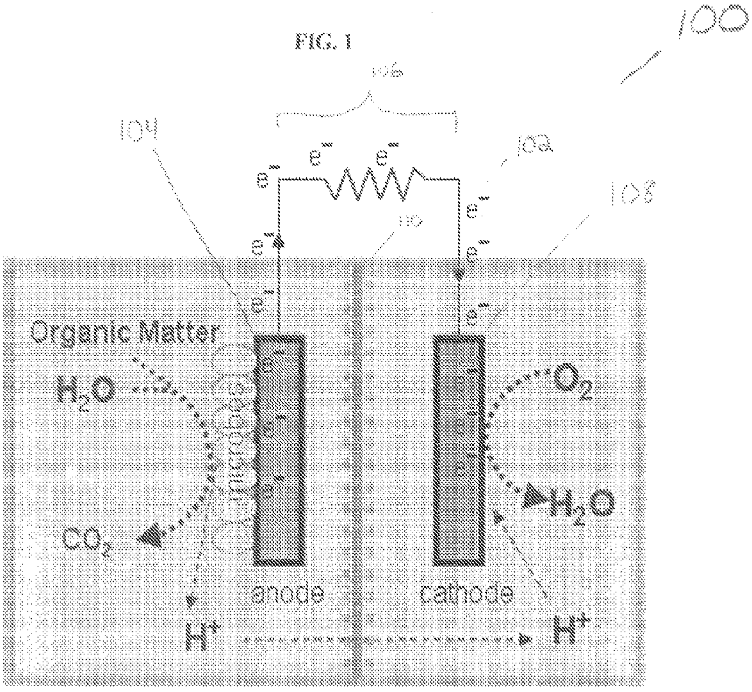
(54) Title: SYSTEMS AND DEVICES FOR TREATING AND MONITORING WATER, WASTEWATER AND OTHER BIODEGRADABLE MATTER

FIG. 1



(57) Abstract: The invention relates to bio-electrochemical systems for the generation of methane from organic material and for reducing chemical oxygen demand and nitrogenous waste through denitrification. The invention further relates to an electrode for use in, and a system for, the adaptive control of bio-electrochemical systems as well as a fuel cell.

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SYSTEMS AND DEVICES FOR TREATING AND MONITORING WATER, WASTEWATER AND OTHER BIODEGRADABLE MATTER

CROSS-REFERENCE TO RELATED APPLICATIONS

This patent application claims the benefit of U.S. Provisional Application Serial No. 61/187469, filed in the U.S. Patent and Trademark Office (USPTO) on June 16, 2009, U.S. Provisional Application Serial No. 61/245085 filed in the USPTO on September 23, 2009, and U.S. Provisional Application Serial No. 61/267594 filed in the USPTO on December 8, 2009, the entire contents of each of these applications being hereby incorporated by reference herein.

TECHNICAL FIELD

The invention generally relates to systems and devices for treating and monitoring water, wastewater and other biodegradable matter, and generating value-added products from such matter.

BACKGROUND INFORMATION

The treatment and monitoring of water is a critical societal need. Approximately three percent (3%) of all electricity produced in the United States is consumed by wastewater treatment infrastructure. Of the electricity produced, approximately one and one-half percent (1.5%) is used in the actual treatment of wastewater. Some existing treatment paradigms include aerobic digestion and anaerobic digestion, however, these paradigms suffer from several drawbacks. For example, aerobic digestion is an energy intensive process and creates significant byproducts, such as bio-solids. In addition, anaerobic digestion cannot treat water to levels low enough for environmental release. These drawbacks keep the cost of wastewater treatment high, which thereby affects a range of industries and municipalities. Thus, there is a critical need for cheaper and more energy efficient wastewater treatment technologies.

Bio-electrochemical systems (BES) are capable of generating electricity or other value-added products from the oxidation and reduction of organic matter. BES consist of electrodes, such as anode and cathodes, both or individually coated in bio-films with the ability to transfer or accept electrons from electrodes. Electrodes may also be coated in noble medals to catalyze one of the reactions taking place. The electrodes can then be separated by an electrolyte which conveys ions between them (generally a membrane).

Electrodes, bio-films, electrolytes, and catalysts may or may not be enclosed in a casing. Each of these elements, which include the casing, can be connected to external circuits, control systems, or other reactors for use in combined systems. The geometrical configuration of the elements in a microbial fuel cell and their material definition can together be defined as the "architecture" of the system.

Over the years, a number of different BES architectures and components have been developed and tested for different uses. Two major categories of architectures are those that operate in batch mode versus flow-through (or plug flow) mode. In a batch-mode system, an oxidant is placed in a reactor in batches and is treated until some endpoint is reached before the next batch is treated. In flow-through mode, a continuous flow of material to be treated is provided into a reactor with a concurrent flow out of the reactor for a constant volume to be retained inside.

Flow through reactors include side-ways flow or upward flow, such as the upflow microbial fuel cell (UMFC) In a UMFC, an organic-laden medium is percolated upwards through a porous anode material (i.e. graphite granules). A number of electrode designs have also been used in UMFC designs. Original UMFC designs used in laboratory tests were not scalable due to the use of flat electrode surfaces, which provided low surface areas per volume of reactor. Therefore, high surface area materials were developed, called a "brush anode", consisting of small-diameter graphite fibers linked to a central core (generally a non-corrosive metal such as titanium) that provides both high conductivity as well as resistance to fouling. Brush anodes have been made of carbon fibers (e.g. PANEX®33 160K) and cut to a set length and wound using an industrial brush manufacturing system into a twisted core consisting of two titanium wires. When placed in a reactor, the total surface area of typical brush electrodes per volume of reactor has been estimated to be as high as 9600 m2/m3. Reactors using these brushes have produced up to 2400 mW/m2 in a cube reactor with a defined acetate medium . However, these electrodes are expensive due to the materials used. In addition, the form itself, a wrapped brush, requires several steps to manufacture.

Therefore, a need exists to address the aforementioned drawbacks of the prior art.

SUMMARY OF THE INVENTION

In one aspect, the invention relates to a bio-electrochemical system for the generation of methane from organic material. The system is comprised of a reactor that includes an anode, a cathode, a methanogenic microbe, and a power source configured to apply voltage to the anode and the cathode. The anode and the cathode are substantially in proximity within the reactor.

In one embodiment according to this aspect of the invention, the voltage facilitates exocellular electron transfer from the anode to the cathode. In another embodiment according to this aspect of the invention, the system is further comprised of a plurality of methanogenic microbes. In another embodiment according to this aspect of the invention, the voltage facilitates exocellular electron transfer to methanogenic microbes to initiate a reduction of hydrogen-2 oxidation. In yet another embodiment according to this aspect of the invention, methane is generated and organic materials are oxidized at either or each of the anode and cathode. The generation of methane and the oxidation of organic materials serve as the purpose of controlling elements within the reactor. The controlling elements include any one or more of the following: the measure of pH, biochemical oxygen demand, chemical oxygen demand, ammonia, and other chemical species. In another embodiment according to this aspect of the invention, the reactor is an existing anaerobic digestion system used for wastewater and solids treatment. The anode and the cathode are placed within the anaerobic digestion system for the purpose of enhancing methane production or controlling elements of an anaerobic digestion process.

In another embodiment according to this aspect of the invention, the power source is electricity generated by a generator or a fuel cell powered by methane generated in the reactor. In yet another embodiment according to this aspect of the invention, a flow is created within the system to move material from the anode to the cathode to increase the rate of methane production.

In a second aspect, the invention relates to a bio-electrochemical system for reducing chemical oxygen demand and nitrogenous waste through denitrification. The system is comprised of a first chamber, a second chamber, a methanogenic microbe, and a filter disposed between the first chamber and the second chamber. The first chamber includes an anode and the second chamber includes a cathode. The filter is configured to facilitate nitrification produced therein.

In one embodiment according to this aspect of the invention, the first chamber includes a first wall and a second wall defining an enclosed space such that the anode facilitates the oxidization of the microbe. In another embodiment according to this aspect of the invention, the second chamber includes a first wall and a second wall defining an enclosed space such that the cathode is configured to facilitate the reduction of nitrates, oxygen or other oxidized species.

In yet another embodiment according to this aspect of the invention, the first chamber has a substantially tubular configuration. In another embodiment according to this aspect of the invention, the system further comprises a membrane for separating the first chamber and the second chamber. In another embodiment according to this aspect of the invention, the first chamber is disposed within a first membrane and the second chamber is disposed around the first membrane and enclosed by a tube member. In yet another embodiment according this aspect of the invention, the filter is a trickling filter that is placed above the anode to facilitate flow through the anode and over the trickling filter.

In a third aspect, the invention relates to an electrode for use in a bio-electrochemical system. The system includes a first surface and a second surface. The first surface is comprised of a substantially conductive material. The conductive material is woven to the second surface.

In one embodiment according to this aspect of the invention, a membrane is disposed between the first surface and the second surface. In another embodiment according to this aspect of the invention, the conductive material is woven to the second surface using carpet-manufacturing techniques and technologies. In yet another embodiment according to this aspect of the invention, the conductive material is carbon fiber. In another embodiment according to this aspect of the invention, the first surface has a substantially tubular configuration. In another embodiment according to this aspect of the invention, the second surface has a substantially tubular configuration. In yet another embodiment according to this aspect of the invention, the electrode further comprises a plurality of first and second surfaces. In yet another embodiment according to this aspect of the invention, the electrode further comprises a plurality of membranes.

In a fourth aspect, the invention relates to a system for the adaptive control of a bio-electrochemical system. The system includes a probe configured to measure stimulus emitted to a fuel cell, and a control tool for monitoring levels of the fuel cell. The control tool is also configured to optimize the levels of the fuel cell.

In one embodiment according to this aspect of the invention, the control tool monitors a plurality of chambers within the fuel cell. In another embodiment according to this aspect of the invention, the stimulus includes any one or more of the following: voltage, current, pH, temperature, internal resistance, activation voltage loses, concentration voltage loses, fuel concentration, ammonia levels, nitrate levels, oxygen levels, and oxygen levels. In another embodiment according to this aspect of the invention, the levels include any one or more of the following: voltage, resistance, electrode spacing, fuel loading rate, and pH of fuel.

In a fifth aspect, the invention relates to a fuel cell. The fuel cell is comprised of a first compartment including a cascading anode, a second compartment including a cascading cathode, and a plurality of inputs and outputs within each of the first chamber and the second chamber.

In one embodiment according to this aspect of the invention, the fuel cell includes a substantially tubular configuration in which methanogenic or electrogenic microbes are disposed therein. In another embodiment according to this aspect of the invention, the first compartment is disposed within the second compartment. In yet another embodiment according to this aspect of the invention, the first and second compartments are disposed within a third compartment including an air-cathode.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings, like reference characters generally refer to the same or similar parts throughout the different views. Also, the drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention.

FIG. 1 is a plan view of a bio-electrochemical system, in accordance with the present disclosure.

FIG. 2 is a plan view of an embodiment of a bio-electrochemical system, in accordance with the present disclosure.

FIG. 3 is a plan view of another embodiment of a bio-electrochemical system, in accordance with the present disclosure.

FIG. 4A is a perspective view of a fuel cell for use in a bio-electrochemical system, in accordance with the present disclosure.

FIG. 4B is a perspective view of an embodiment of a fuel cell for use in a bio-electrochemical system, in accordance with the present disclosure.

FIG. 5A is a plan view of an embodiment of a fuel cell for use in a bio-electrochemical system, in accordance with the present disclosure.

FIG. 5B is a plan view of an embodiment of a fuel cell for use in a bio-electrochemical system, in accordance with the present disclosure.

FIG. 6 is a perspective view of an embodiment of a fuel cell for use in a bio-electrochemical system, in accordance with the present disclosure.

FIG. 7 is a perspective view of an embodiment of a fuel cell for use in a bio-electrochemical system, in accordance with the present disclosure.

FIG. 8 is a plan view of an embodiment of a fuel cell for use in a bio-electrochemical system, in accordance with the present disclosure.

FIG. 9A is a top view of an embodiment of a fuel cell for use in a bio-electrochemical system, in accordance with the present disclosure.

FIG. 9B is a cross-sectional view of an embodiment of a fuel cell for use in a bio-electrochemical system, in accordance with the present disclosure.

FIG. 10 is a plan view of a fuel cell for use in a bio-electrochemical system, in accordance with the present disclosure.

DESCRIPTION

Different bio-electrochemical system configurations have been devised to create a number of value-added end products. Two of the most important are electricity and hydrogen gas. Referring to Figure 1, in a bio-electrochemical system 100, electrical current can be created by harvesting electrons 102 liberated during microbial breakdown of organic wastes at an anode 104 while allowing the electrons 102 to flow through a circuit 106 to a cathode 108 exposed to a terminal electron acceptor, usually oxygen. Hydrogen can be generated by purposely applying a voltage to the system 100 while using water as the cathode electron acceptor, which enables hydrogen evolution at the cathode.

In almost all instantiations of microbial fuel cells, the architecture has been such that the anodic and cathodic compartments are separated by a barrier 110. Often the barrier 110 is an electrically conductive membrane that can selectively allow ions to pass through it. Conversely, the fluid in the system 100 can be used as the electrolyte in a membraneless configuration. However, in this latter instantiation, an electron acceptor must be provided, and therefore a region is created where the cathode 108 can either be exposed to the air, or pass the fuel/eletrolyte over the barrier 110 where it can then come in contact with the cathodic 108 while also exposing it to the air or some electron acceptor.

For example, in all configurations in which hydrogen is created, the cathode 108 is assumed to be co-exposed to a different compartment than the anode 104 for the hydrogen gas to be evolved. Similarly, in another configuration, the electrolyte is passed through a loop into the cathode 108, before which it can optionally undergo exposure to oxygen in the air.

Referring to Figure 2, a bio-electrochemical system 200 for the generation of methane from organic material is presented. The system 200 is comprised of a reactor 202 that includes an anode 204, a cathode 206, and a methanogenic microbe 208. The anode 204 and the cathode 206 are substantial in close proximity to one another within the system 200. The system is further comprised of a power source (not shown in Figure) that is configured to apply voltage to the anode 204 and the cathode 206. The voltage facilitates exocellular electron transfer from the anode 204 to the cathode 206. In addition, the voltage facilitates the reduction of hydrogen-2 oxidation.

In one embodiment, the methanogenic microbe 208 is biodegraded into three principal groups within the system 200. For example, the microbe 208 may be primary fermentors, secondary fermentors, and hydrogenotrophic methanogens. Each of the microbes 208 may occur independently of the anode 204 and the cathode 206 in the system 200, however, the incorporation of the anode 204 and the cathode 206 provides an additional mechanism for hydrogen production and/or electron transport within the system 200. This mechanism provides an enhanced rate of treatment and/or alteration of the composition of the microbe 208.

Methanogenic metabolism from carbon-containing wastes, referred to as anaerobic digestion (AD) due to its requirement of anoxic conditions, is a widely-used organic wastewater remediation technology. Its significant benefits over aerobic waste treatment include the production of methane rich gas (called biogas), lower sludge production, and lower operating costs. These benefits have led to its application to diverse organic waste streams, such as municipal wastewater, agricultural and food processing waste, and chemical industry waste.

Microbe-mediated methane production from complex organic waste streams is a multi-stage process. In the first stage, the acid-former group (acetogens), which contains many sub-niches, includes species that digest polysaccharides, sugars, fatty acids, alcohols and more complex molecules in the waste into organic acids, primarily acetate, but also others like lactate and butyrate. The second class is the methane-formers, or methanogens, which consist of two sub-niches. Some methanogens metabolize acetate directly and produce methane as a byproduct (aceticlastic methanogenesis), while the other methanogens use Hydrogen-2 (H_2) and Carbon Dioxide (CO_2) as energy sources to produce methane (hydrogenotrophic methanogenesis).

Hydrogenotrophic methanogenesis (HM) is a favorable process within the reactor 202 because of the consumption, rather than production, of CO_2 during methane production, which results in a purer biogas with a higher proportion of methane and a lower proportion of CO_2. While CO_2 and acetate are generally abundant byproducts of upstream (acetogenic) metabolic processes, H_2 is a minor byproduct that may quickly become limiting and therefore, aceticlastic methanogenesis (AM) can be used instead of HM under normal anaerobic digestion operation conditions. Additionally, hydrogenotrophic methanogens are more resistant to high temperatures (thermophilic conditions) above 50°C. Referring to Table 1 below, the HM has a lower Gibbs free energy change than the AM reaction and is therefore thermodynamically favored.

Table 1: Routes of methanogenesis.

Reaction	Equation	Free Energy Change $\Delta G°$ (kJ/reaction)
Hydrogenotrophic methanogenesis	$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$	-130.7
Aceticlastic methanogenesis	$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$	-31.0

The system 200 addresses hydrogen limitation in the HM reaction by including within the reactor 202 an electrode, or set of electrodes, such as the anode 204 and the cathode 206, that deliver a voltage to increase the favorability of H_2 formation. In one embodiment, the anode 204 and the cathode 206 directly donate electrons to hydrogenotrophic methanogens to reduce or eliminate the need for H_2 oxidation.

Because the production of hydrogen in the system 200 occurs at the surface of the anode 204 and cathode 206 where methanogenic organism biofilms are present, the production occurs in a scale and location that is more easily available to methanogenic microbes 208 than it would be if the simple mixing of hydrogen gas took place within the reactor 202. Further, the hydrogen production and rapid co-consumption within the system 200 is inherently much safer than the use of bulk hydrogen gas.

In one embodiment, a microbial electrolysis cell is added within the system 200 such that the H_2 evolved at the cathode 206 is produced where methanogenic microbes 208 can immediately utilize it for methane production. This is achieved by the addition of sufficient electrical voltage such that that the cathode 206 potential is negative to allow H_2 formation as a terminal electron acceptor for microbial metabolism. The H_2 that is produced is then utilized by hydrogenotrophic methanogens to produce methane gas more efficiently.

In another embodiment, an electrode, such as the anode 204 or cathode 206, supplying electrons to methanogens microbes 208 is contained in a chamber (not shown in Figure), where the cathode 206 potential is provided such that electrons transferred to methanogens microbes 208 are at a correct energy to allow methane production without the need for hydrogen. In this embodiment, the reactor 202 may be configured as a two chamber reactor, with primary fermentation to produce acetate in the first chamber, and secondary fermentation as well as methanogenesis confined to the second chamber.

In yet another embodiment, hydrogenotrophic methanogenesis is enhanced through the production of H_2 by secondary fermentative organisms accepting electrons from the cathode 206. Additionally, the methanogens microbes 208 undergo direct electron acceptance from the cathode 206 to increase the rate of methane production.

The system 200 may be applied to any anaerobic digestion systems in order to improve the efficiency, rate of treatment, composition or purity of biogas produced, or effective wastewater biochemical oxygen demand (BOD) content range. The system 200 can be applied to a wide range of wastewaters and organic matter streams, including, but not limited to, animal manures or manure slurries; non-manure agricultural wastes;

slaughterhouse waste or wastewater; food processing wastewater or slurries; beverage processing wastewaters, including brewery wastewater or slurries; municipal wastewater; and septic system wastewater or grey-water building wastewater. The system 200 can also be applied to existing technology through a retrofit installation, either as a custom fabricated system or the application of one or more modular electrode enhancement units. Electrode enhancement may also be applied to newly constructed AD systems as a retrofit system or as an integral system component.

Referring to Figure 3, a bio-electrochemical system 300 for reducing chemical oxygen demand and nitrogenous waste through denitrification is presented. The system 300 includes a first chamber 302, a second chamber 304, and a filter 306 disposed between the first chamber 302 and the second chamber 304. The filter 306 is configured to facilitate nitrification therein. The first chamber 302 includes an anode 308. The second chamber includes a cathode 310. Methanogenic microbes 312 are disposed within the first chamber 302 and the second chamber 304. The first chamber 302 is configured to facilitate the oxidization of the microbes 312 therein. In addition, the second chamber 304 is configured to facilitate the reduction of nitrite therein. Each of the first chamber 302 and the second chamber 304 may be separated by a membrane 314.

In one embodiment, the system 300 is comprised of four parts: 1) the first chamber 302 for microbial BOD oxidation; 2) the trickling filter 306 for nitrification of ammonia and nitrite; 3) The second chamber 304 for microbial reduction of nitrate to N_2; and 4) the semi-permeable membrane 314 that separates the first chamber 302 and the second chamber 304 topologically, but retains them in electronic and ionic communication. The system 300 is used to treat wastewater traveling in one direction through the reactor, in either a continuous or intermittent stream.

The first component of the system is the first chamber 302 that contains an electrode or series of electrodes that serve as the attachment point for one or more species of microbes 312. The microbes 312 on these electrodes affect the oxidation of carbon based wastes to reduce the biological oxygen demand (BOD) content of the waste and the transfer of liberated electrons to the anode. There may be one or more first chambers that are arranged in series or in parallel configuration.

The second component of the system is the aerobic trickling filter 306 that is filled with air or other oxygen-containing gas, and contains non-conductive, high-surface area substrate over which wastewater exiting the first chamber 302 can be trickled. Trickling allows rapid re-oxygenation of wastewater for oxidation of ammonia and nitrite to nitrite, also referred to as nitrification. This filter 306 may or may not include a control system for dynamic monitoring of oxygen concentration and for adjustment of oxygen concentration to within an optimal range. In addition, the filter 306 may or may not contain an oxygen-removing device where the wastewater exits the system and enters the third compartment.

The third component of the system is the second chamber 304 that contains an electrode or series of electrodes that serve as the attachment point for one or more species of microbes 312. The microbes 312 on these electrodes affect the acceptance of electrons and the reduction of nitrate in the wastewater to N_2 gas which will diffuse out of the liquid upon exit of water from the system 300. There may be one or more second chambers 304 that are arranged in series or in parallel configuration.

The fourth component of the system is the membrane 314 that topologically separates the first chamber 302 and the second chamber 304. The membrane 314 is permeable to protons and small positive ions, but is impermeable to negative ions and uncharged particles. The membrane 314 serves to keep the first chamber 302 and the second chamber 304 in electrical communication in order to complete the circuit, but does not allow the passage of wastewater components to bypass the system 300.

It is contemplated that the balancing of a number of facets is useful to effect optimal performance of the system 300. These facets include: (1) the ratio of the first chamber 302 to the second chamber 304 volume and number of chambers either arranged in parallel or in series; the ratio of the anode 308 to the cathode 310 electrode surface areas; the flow rate of wastewater through the system 300, as well as continuous vs. intermittent waste flow; the concentration of oxygen and composition of gas within the trickling filter 306, as well as dynamic addition of oxygen to the filter 306; the volume ratios of the first chamber 302 to the trickling filter 306 and the second chamber 312 to the trickling filter 306; and the use of computer-controlled system for dynamic monitoring and adjustment of flow rate, oxygen concentration or oxygen addition to the system 300.

In one embodiment, the system 300 can be used to treat wastes that are carbon:nitrogen imbalanced and therefore require carbon, or possibly nitrogen, additions for efficient remediation by other technologies. These wastes include aquaculture wastes, mariculture wastes, agricultural wastes, food processing and beverage processing wastewaters, and other wastes that are carbon:nitrogen-unbalanced. The system 300 may be used on either recirculating or flow through aquaculture operations.

In another embodiment, microbe 312 co-removal of organic and nitrogen-containing wastes within the system 300 requires carbon to nitrogen ratios of 10:1 to 20:1 to proceed efficiently. Many wastes that are nitrogen-rich do not readily lend themselves to co-treatment. Aquaculture wastes are an important example of this type of unbalanced waste, and their balanced treatment is made more imperative by the effects of ammonia, nitrite and nitrate toxicity on cultured animals. Ammonia and nitrite are toxic at levels well below 1 mg/L, but are readily treated through an aerobic bacterial nitrification process. However, while nitrate levels of 1000 mg/L are tolerable for many species, it is generally advised to keep nitrates below 1000 mg/L in freshwater or 1500 uM (about 93 mg/L) in seawater, as they are detrimental to marine invertebrates in closed systems. The resulting decrease in fish growth rate can cost an aquaculture facility up to several millions of dollars per year.

Where nitrate levels are unacceptably high, water can be denitrified by water exchange or by anaerobic bacteria in a separate treatment system. Anaerobic de-nitrification uses heterotrophic bacteria such as Pseudomonas and an additional carbon source such as methanol to reduce nitrate to nitrite and eventually to nitrogen gas. This method is effective but requires carbon source input and frequent chemical balance monitoring for efficient nitrate removal. Organic matter (e.g. sludge) from the same facility can be used in the place of methanol. However, because the sludge is often in particulate form, hydrolysis and fermentation must be applied to convert the sludge into volatile fatty acids and other molecules more easily consumed by denitrifying organisms, adding complexity and cost to the operation.

Alternatively, the facility can use electrochemically generated hydrogen gas as electron donor to drive biological de-nitrification. This requires constant input of hydrogen gas bought externally or created locally using energy-intensive electrolysis. Another proven approach involves the use of plants in artificial wetlands or hydroponic systems to remove excessive nitrate. The latter adds complexity to the aquaculture system and is not widely used. For these reasons, many farms to date have ignored the affects of nitrates in order to save money on treatment, or used water exchange as the principal form of de-nitrification.

A number of benefits make the system 300 particularly compelling for treatment of carbon:nitrogen-unbalanced wastes, such as aquaculture wastes. First, a preliminary study suggested that a combined BOD/de-nitrification reactor run together with a nitrification step. This achieved increased removal yields of 2 kg COD/m3day, 0.41 kg NO3--N/m3day, with a current generation of 34.6 W/m3, all normalized to the net cathodic compartment, and equally important, they achieved a COD/N ratio of approximately 4.5 g COD/g N. Since, anodic BOD reduction may occur at a fraction of sludge production versus aerobic treatment processes, thereby reducing overall treatment costs significantly. Therefore, each of the first compartment 302 and the second compartment 304 creates an environment with intensive competition for nutrients and substrate attachment sites. These conditions allow probiotic (beneficial) microbes 312, which are more suited to such environments, to survive while fostering a significant reduction in pathogen levels and improvements in fish health within the system 300.

A number of factors may suggest that BOD removal can be achieved using carbon:nitrogen-unbalanced wastes, such as aquaculture wastes at the anode 302. First, as described above, necessary bacteria are already present in wastes. For example, one study showed a reduction of up to eighty-four percent (84%) of the BOD from cow manure slurry, while another study consistently achieved BOD reduction of eighty-percent (80%) using domestic wastewater. Further, another study demonstrated that swine waste could produce electricity in a microbial fuel cell system (MFC) at power densities consistent with other potential substrates using air-cathode MFC systems. These systems measured a maximum power density of 261 mW/m2 while reducing soluble chemical oxygen demand (COD) by 88%-92% percent and ammonia by 83%. Additionally, a number of electrogenic bacteria isolated from freshwater and marine sediments, demonstrating that these species thrive in aquaculture system conditions.

BOD reduction within system 300 is accomplished with significantly less excess biomass production compared to equivalent aerobic processes. Under aerobic conditions, the consumption of 1g of organic substrate produces around 0.4 g of biomass; in an MFC the same amount of BOD reduction proceeds with 50-80% less biomass production observed. One study documented even lower biomass yields in an MFC process under certain conditions. Given that sludge treatment at a municipal waste treatment facility can cost $1,000 per ton of dry waste, this could amount to a substantial reduction in cost and a more favorable cost balance for the BEC process.

Many early studies of BEC processes focused on anodic processes, using traditional platinum-coated, open-air cathodes. One study noted bio-cathodic oxygen reduction in open-sea systems. Another study demonstrated high current production using an acetate-fed fuel cell with a graphite felt open-air biological cathode 83±11 W m-3 MFC (0.183 L MFC) for batch- fed systems (20-40% coulombic yield) and 65±5 W/m-3 MFC for a continuous system with an acetate loading rate of 1.5 kg COD m-3 day-1 90±3% coulombic yield). These study found that by adding manganese to air-cathode, power output increased substantially. Other studies confirmed cathodic bacteria's role as a true oxygen catalyst.

Biological cathodes reduced electrode cost by avoiding previous metal catalysts. Perhaps as importantly for water treatment applications, biological reduction can be harnessed to perform additional treatment steps. De-nitrification is a prime target because the reduction potential on the order of that of oxygen (NO_3-/N_2 at +0.74V versus +0.82V for O_2/H_2O). One study was able to demonstrate increased denitrification in the presence of biological cathodes (55.1% increase at 100-200mV and current of 40mA), though this was accomplished using poised potentials rather than full MFC processes. More recently, combined BOD/de-nitrification was demonstrated in complete microbial fuel cell systems operating with biological cathodes.

Another proposed study recently demonstrated a combined BOD/de-nitrification reactor running together with a nitrification step. This study achieved increased removal yields of 2 kg COD/m3day, 0.41 kg NO3--N/m3day, with a current generation of 34.6 W/m3 all normalized to the net cathodic compartment. Equally important, the study achieved a COD/N ratio of approximately 4.5 g COD/g N, as compared to the typical requirement ratio of 7, a value which virtually eliminates the need for carbon addition in wastewater treatment. The system 300 combines the concept of looping nitrification together with other advances made in the field to achieve an economically superior combined carbon-nitrogen treatment.

In one embodiment, the system 300 is a two-chamber system (the first chamber 302 and the second chamber 304), where the anode 308 and the cathode 312 are separated into two chambers by the membrane 314 that allows ion exchange. In another embodiment, the system 300 is a single chamber system using air at the cathode 312, which can utilize either a chemical catalyst or a biologically-catalyzed cathode.

Both single and two-chamber systems can be operated in batch or flow-through mode. A variation on the flow-through MFC, called an upflow MFC (UMFC), addresses transport limitations and it has been shown to operate with lowered internal resistance than a conventional MFC. In the UMFC, organic-laden medium 312 is percolated upwards through a porous anode 312 material (i.e. graphite granules). In one study, the MFC was partitioned with a proton exchange membrane, placing an air-exposed cathodic chamber above the anode 308. In this study, defined sucrose medium was used to test the UMFC. High SCOD removal rates were observed (up to 97%) even at relatively high loading rates over 3 g COD/L/day, though a majority of this could be attributed to methanogenesis rather than electron transport. A second study undertaken with another UMFC design showed that a lower internal resistance increased volumetric power production to a maximum of 27 W/m3. More recently, a pilot scale upflow MFC was developed and demonstrated by running on brewery effluent.

Referring now to Figures 4A, 4B, 5A, 5B, 6, 7, 8, 9A, and 9B, an electrode 400 for use in a bio-electrochemical system is presented. The electrode 400 includes a first surface 402 and a second surface 404. The first surface is comprised of substantially conductive material 406 that is woven to the second surface 404. A membrane 408 may be disposed between the first surface 402 and the second surface 404. The conductive material 406 may be, for example, carbon fiber. In one embodiment, as shown in Figure 5A, the first surface 402 has a substantially tubular configuration. In another embodiment, as shown in Figure 5B, the second surface 404 has a substantially tubular configuration. As shown in Figures 6 and 7, the electrode 400 may also include a plurality of first and second surfaces as well as a plurality of membranes.

The electrode 400 may be comprised fabricated from any material 406 with suitable physical and electrical properties. These properties include, but are not limited to, electrical conductivity, flexibility/stiffness, catalytic properties, and biological compatibility. The base weave of the material 406 may be made of a different material from its loops or tufts. For example, a different material may be used because it is cheaper and/or a better conductor of electricity. Additionally, a base material 406 may be used for the electrode 400 with a specialty coating layer applied to enhance the electrode's 400 performance.

The electrode 400 may also be made from a variety of sizes. The shape of the electrode 400 may be varied as well. The electrode 400 may include several characteristic dimensions, such as length, width, depth, fabric weave size (grid spacing), and tuft/loop spacing and density. These dimensions will have direct impact on the performance of the electrode 400 and will be optimized to meet the specific demands of the electrode 400. Further, any type of construction technique may be used for the fabrication of the electrode 400. These techniques include, but are not limited to, needle punching, tufting, axminster, durcam, woven, knitted, rivet head, fusion bonded, and flocked. The specific construction technique used will depend on the materials and exact specifications of the electrode 400.

In one embodiment, the electrode 400 may be provide with a dielectric material 406 in order to divide the electrode 400 into different chambers. The material 406 can serve to selectively allow the transmission of certain soluble chemicals on the basis of size, hydrophobicity, charge, and other properties. The material 406 may be, for example, a sheet polymeric membrane. In order to minimize system space, the membrane may be adhered directly onto the bottom of the electrode 400. This material 406 provides structural support as well as physical separation and selective transport. In another embodiment,

For the case of a fuel cell in which ion transport is essential, minimization of distance from the electrode to the selectively permeable membrane decreases the distance, time, and driving force required for diffusion. Therefore, in another embodiment, this construct can be used without modification in planer geometry and can be used in combination with any other type of electrode 400.

Referring to Figure 5A, the electrode 400 is comprised of a substantially tubular configuration. This configuration may be accomplished by rolling the material 406 with the second surface 404 on the exterior, thereby creating an external tubular electrode 400. This provides for compartmentalization, which is useful in many reactor configurations. A use of this construct would be to use one side of the electrode 400 (inside or outside) as a cathode and the other side as the anode in a fuel cell.

In one embodiment, the electrode 400 can be utilized in a system that is either batch or continuous. The working fluid on either side of the membrane may be gaseous or liquid. The liquid may flow from one section into the other or have no connection. The flow may be in the same or opposite directions and the tube may be oriented in any desired direction. With the external tubular electrode 400, any other electrode may be used on the inside of the electrode 400.

Referring to Figure 5B, like the electrode of Figure 5A, the electrode 400 is comprised of an internal tubular architecture by rolling the material 406 with the first surface 402 on the interior. Electrode 400 provides for compartmentalization and its use is similar to the electrode of Figure 5A.

Referring to Figure 6, the electrode 400 may be modified to incorporate additional electrodes by placing additional electrode(s) 410 on the back side of the first layer 402. Thus, the back side of the first layer 402 becomes an intermediate layer 408. The dielectric material 406 provides the same functions (support, containment, selective transport) as the electrode of Figure 5A, but also provides direct electric insulation to the electrode 400 to avoid a short circuit between the two electrodes. Either electrode can still be used for any desired reaction. The architecture of the electrode 400 and the electrode 410 minimize the distance between the two electrodes for accelerated ion transport while simultaneously maximizing the surface area of the electrode. Electron donation occurs at one electrode while electron accepting occurs at the other electrode. It is contemplated that the electrical potential of the donating electrons does not need to be higher than that of the accepting electrons if a power source is placed between the electrodes.

Referring to Figure 7, the electrode 400 may include multiple layers of stacked electrodes to form a series of chambers. In one embodiment, the anode and cathode (not shown in Figure) electrode 400 reside in the same chamber throughout the surface of the electrode 400. Specifically, the same type (anode or cathode) can be wired together or separately depending on the reactor performance. Electrode 400, can facilitate flow in any direction and has the benefit of large surface area, high throughput, and the capability of achieving a higher volume without sacrificing close electrode spacing.

Referring to Figure 8, the electrode 400 may have a substantially tubular configuration such that either side of the electrode 400 may be used as a cathode or anode. Further, electrode 400 may be operated in a batch or continuous flow, its orientation may be in any direction, and it may utilize liquid or gas in either its first layer or second layer. It is contemplated that multiple electrodes 400 may be connected in series or parallel. The wiring may connect the electrodes 400 and the different sections depending on the specific application. Further, the concentric electrode 400 may be used with or without an exterior casing, depending on the specific application.

In another embodiment, the incorporation of multiple concentric electrodes 400 into a single reactor results in the production of a shell and tube electrode reactor. This reactor may contain any number of electrodes 400 contained within the shell. As with any shell and tube reactor, the flow may co-flow, counter-flow, or cross-flow. Further, both the tube and the shell side may contain as many passes as desired. Flow may be connected between the two electrodes 400 or unconnected. In addition, the sections and different electrodes 400 may be wired as needed. The shell and tube electrode reactors makes full utilization of space by packing as much reactive surface area as possible into the smallest volume.

Electrode 400 may find a variety of applications. In one embodiment, the high specific surface area makes the electrode 400 ideal for fuel cell applications. Fuel cells are often limited by the area available to catalyze the reaction and by sizes which can be used while maintaining efficiency. The electrode 400 simultaneously maximizes surface area and minimizes electrode separation, thus optimizing the fuel cell. Electrodes 400 are suitable for use in all types of fuel cells. The material of the electrode 400 needs to be selected with the specific electrode and application in mind.

In another embodiment, the electrode 400 may be utilized to increase the productivity of batteries. If the battery is limited by the rate of the electrode, the electrode 400 may increase current. Electrode 400 may also be used for any reaction which requires separated oxidation and reduction steps. Any reactor which makes use of a redox reactor has the possibility to be utilized with the electrode 400. This allows for separation of the half reactions which may allow energy extraction or minimization of energy input. Additionally, this may limit the formation of by-products from side reactions. In addition, the natural compartmentalization of a reactor utilizing the electrode 400 carries the benefit of reduced separations requirement. The electrode 400 is capable of providing electrons (with or without associated ions) into a well-defined environment, thus enhancing the chemical purity of the product. Alternatively, the electrode 400 can act as an electron sink to remove electrons from a system.

In yet another embodiment, biological catalysis may be used with the electrode 400. The electrode 400 maximizes the surface available for microbial attachment. In this application, electrode materials are chosen to be biocompatible with specific attention to attachment properties. Microbial fuel cells are one application of biological catalysis with the electrode 400, but this is not the only process. Biology, especially microbiology, has an extremely diverse set of metabolic capabilities. These unique and efficient processes can be utilized in a reactor with the electrode 400 to produce and convert not only energy but also a wide variety of chemicals from simple to complex.

Further, any application which utilizes an electrode for the transfer of electrons may utilize the electrode 400. More complex devices building upon electrodes may be also constructed with the electrode 400.

Referring to Figure 10, a fuel cell 500 is presented. The fuel cell 500 is comprised of a first compartment 502, a second compartment 504, a third compartment 506, and a plurality of inputs and outputs within each of the first compartment 502 and the second compartment 504.

The first compartment 502 includes a cascading anode electrode and the second compartment 504 includes a cascading cathode electrode. The fuel cell 500 may have a substantially tubular configuration. In addition, the first compartment 502 may be disposed within the second compartment 504. Further, the first compartment 502 and the second compartment 504 may be disposed within a third compartment 504, which includes an air-cathode.

Fuel cell 500 may be designed for use with existing anaerobic digester (AD) systems. For example, the fuel cell 500 can create a cascading series of electrogenic enhanced AD reactors in which the placement of electrodes, applied voltages, and other attributes of the fuel cell 500 are designed to optimize methane production. In one embodiment, the cascading chambers can be designed to alternate between anode and cathode electrodes. For example, the chambers may be designed to alternate between biological anodes or cathodes and chemical anodes or cathodes. Each compartment of the fuel cell 500 may have a different applied voltage, thereby enabling more complete wastewater treatment at lower cost.

In one embodiment, two electrodes may be used with the fuel cell 500 to retrofit with existing anaerobic digesters by taking the power from a generator to enhance anaerobic digestion, both in terms of the speed of the process and the level to which water may be treated. Because exo-electric bacteria oxidizes organics in wastewater to lower levels than methanogensis, the fuel cell 500 can clean more water using this process than with standard AD systems.

In another embodiment, the fuel cell 500 may control the pH of flow within its compartments. This process may be accomplished by modulating the applied voltage, and other aspects of the fuel cell 500 to ensure the pH remains in the right range for anaerobic digestion, thus optimizing methane production. Further, this pH modulation can be used in combination with another bio-electrochemical system using computers and measurements from the elements of the fuel cell 500.

In another aspect of the invention, a system for the adaptive control of a bio-electrochemical system is presented. The system is comprised of a probe configured to measure stimulus emitted to a fuel cell and a control tool for monitoring levels of the fuel cell. The stimulus may be, for example, any one or more of the following: voltage, current, pH, temperature, internal resistance, activation voltage loses, concentration voltage loses, fuel concentration, ammonia levels, nitrate levels, oxygen levels, and oxygen levels. The control tool is configured to optimize the levels of the fuel cell. The levels may include any one or more of the following: voltage, resistance, electrode spacing, fuel loading rate, and pH of fuel.

It is contemplated that the system can be used to tune various zones of a fuel cell independently. In one embodiment, the system further includes multiple resistors. The system also includes automated feedback control which can be used to maintain various levels within the system. For example, the automated feedback control allows control over the appropriate pH in an operation of a traditional anaerobic digester, or an enhanced anaerobic digester. The pH change can be implemented by changing some aspect of the bio-electrochemical system and thus the rate at which it operates, such as the resistance between electrodes or the applied voltage. In another embodiment, the activity of the bio-electrochemical system can be used to sense and monitor pH through the use of buffers, such as lime for enhanced performance.

It will be understood that various modifications may be made to the embodiments disclosed herein. Therefore, the above description should not be construed as limiting, but merely as illustrative of some embodiments according to the invention.

WHAT IS CLAIMED IS:

1. A bio-electrochemical system for the generation of methane from organic material, comprising:

a reactor including an anode, a cathode, and a methanogenic microbe, the anode and the cathode in substantial proximity therein; and

a power source configured to apply voltage to the anode and the cathode.

2. The system of claim 1, wherein the voltage facilitates exocellular electron transfer from the anode to the cathode.

3. The system of claim 1, further comprising a plurality of methanogenic microbes.

4. The system of claim 1, wherein the voltage facilitates exocellular electron transfer to the methanogenic microbes to initiate a reduction of hydrogen-2 oxidation.

5. The system of claim 1, wherein methane is generated and organic materials are oxidized at either or each of the anode and cathode.

6. The system of claim 5, wherein the generation of methane and the oxidation of organic materials serve as the purpose of controlling elements within the reactor.

7. The system of claim 6, wherein the controlling elements include any one or more of the following: the measure of pH, biochemical oxygen demand, chemical oxygen demand, ammonia, and other chemical species.

8. The system claim 1, wherein the reactor is an existing anaerobic digestion system used for wastewater and solids treatment.

9. The system of claim 8, wherein the anode and the cathode are placed within the anaerobic digestion system for the purpose of enhancing methane production or controlling elements of an anaerobic digestion process.

10. The system of claim 1, wherein the power source is electricity generated by a generator or a fuel cell powered by methane generated in the reactor.

11. The system of claim 1, wherein a flow is created within the system to move material from the anode to the cathode to increase the rate of methane production.

12. A bio-electrochemical system for reducing chemical oxygen demand and nitrogenous waste through denitrification, comprising:

a first chamber including an anode;

a second chamber include a cathode;

methanogenic or electrogenic microbes; and

a filter disposed between the first chamber and the second chamber, the filter configured to facilitate nitrification produced therein.

13. The system of claim 12, wherein the first chamber includes a first wall and a second wall defining an enclosed space such that the anode facilitates the oxidization of the microbes.

14. The system of claim 12, wherein the second chamber includes a first wall and a second wall defining an enclosed space such that the cathode is configured to facilitate the reduction of nitrates, oxygen or other oxidized species.

15. The system of claim 12, wherein the first chamber has a substantially tubular configuration.

16. The system of claim 12, further comprising a membrane for separating the first chamber and the second chamber.

17. The system of claim 12, wherein the first chamber is disposed within a first membrane and the second chamber is disposed around the first membrane and enclosed by a tube member.

18. The system of claim 12, wherein the filter is a trickling filter that is placed above the anode to facilitate flow through the anode and over the trickling filter.

19. An electrode for use in a bio-electrochemical system, comprising:

a first surface and a second surface, the first surface comprising a substantially conductive material, wherein the conductive material is woven to the second surface.

20. The electrode of claim 19, wherein a membrane is disposed between the first surface and the second surface.

21. The electrode of claim 19, wherein the conductive material is woven to the second surface using carpet-manufacturing techniques and technologies.

22. The electrode of claim 19, wherein the conductive material is carbon fiber.

23. The electrode of claim 19, wherein the first surface has a substantially tubular configuration.

24. The electrode of claim 19, wherein the second surface has a substantially tubular configuration.

25. The electrode of claim 19, further comprising a plurality of first and second surfaces.

26. The electrode of claim 19, further comprising a plurality of membranes.

27. A system for the adaptive control of a bio-electrochemical system, comprising:

a probe configured to measure stimulus emitted to a fuel cell; and

a control tool for monitoring levels of the fuel cell, the control tool further configured to optimize the levels of the fuel cell.

28. The system of claim 27, wherein the control tool monitors a plurality of chambers within the fuel cell.

29. The system of claim 27, wherein the stimulus includes any one or more of the following: voltage, current, pH, temperature, internal resistance, activation voltage loses, concentration voltage loses, fuel concentration, ammonia levels, nitrate levels, oxygen levels, and oxygen levels.

30. The system of claim 27, wherein the levels include any one or more of the following: voltage, resistance, electrode spacing, fuel loading rate, and pH of fuel.

31. A fuel cell, comprising:

a first compartment including a cascading anode;

a second compartment including a cascading cathode; and

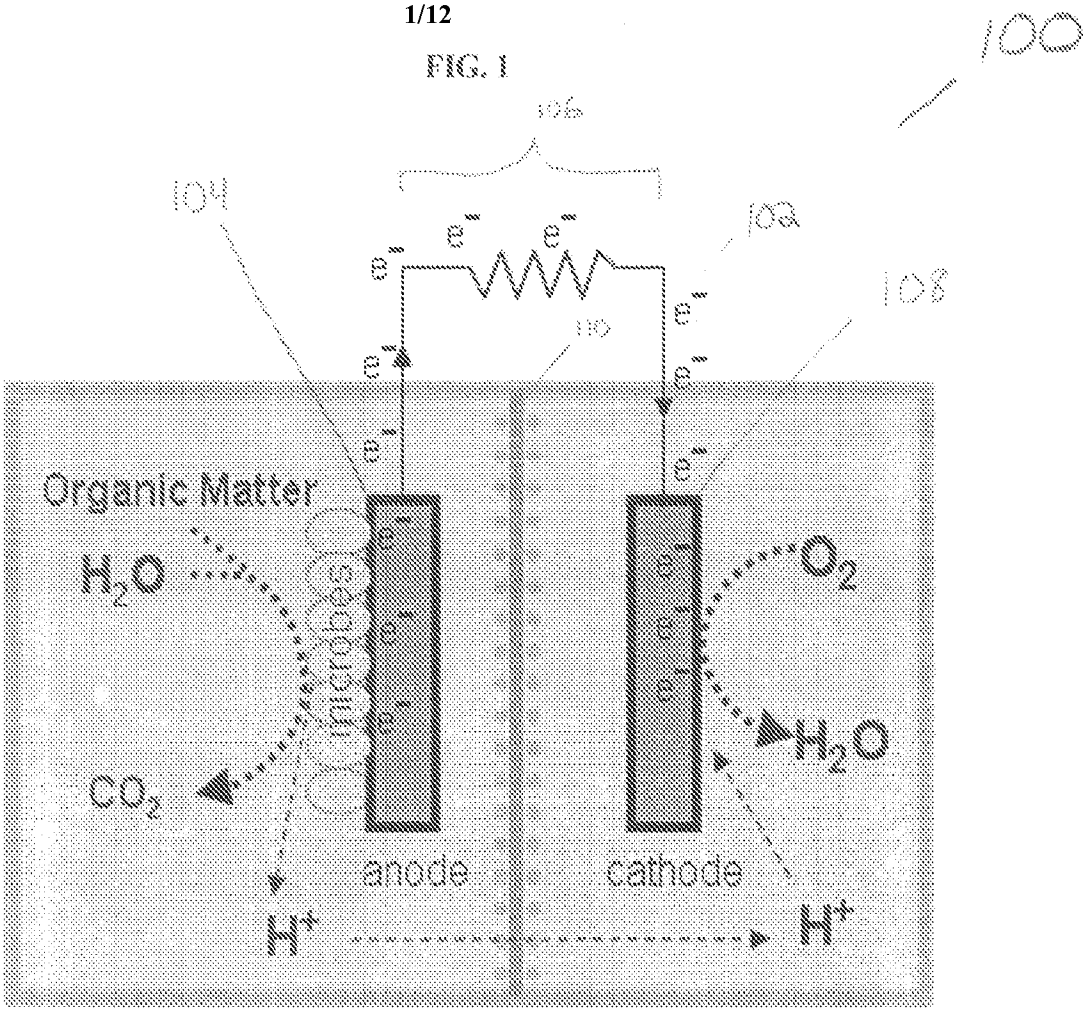
a plurality of inputs and outputs within each of the first chamber and the second chamber.

32. The fuel cell of claim 31, wherein the fuel cell includes a substantially tubular configuration in which methanogenic or electrogenic microbes are disposed therein.

33. The fuel cell of claim 31, wherein the first compartment is disposed within the second compartment.

34. The fuel cell of claim 33, wherein the first and second compartments are disposed within a third compartment including an air-cathode.

FIG. 1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104
102
108
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e⁻
e⁻
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Organic Matter
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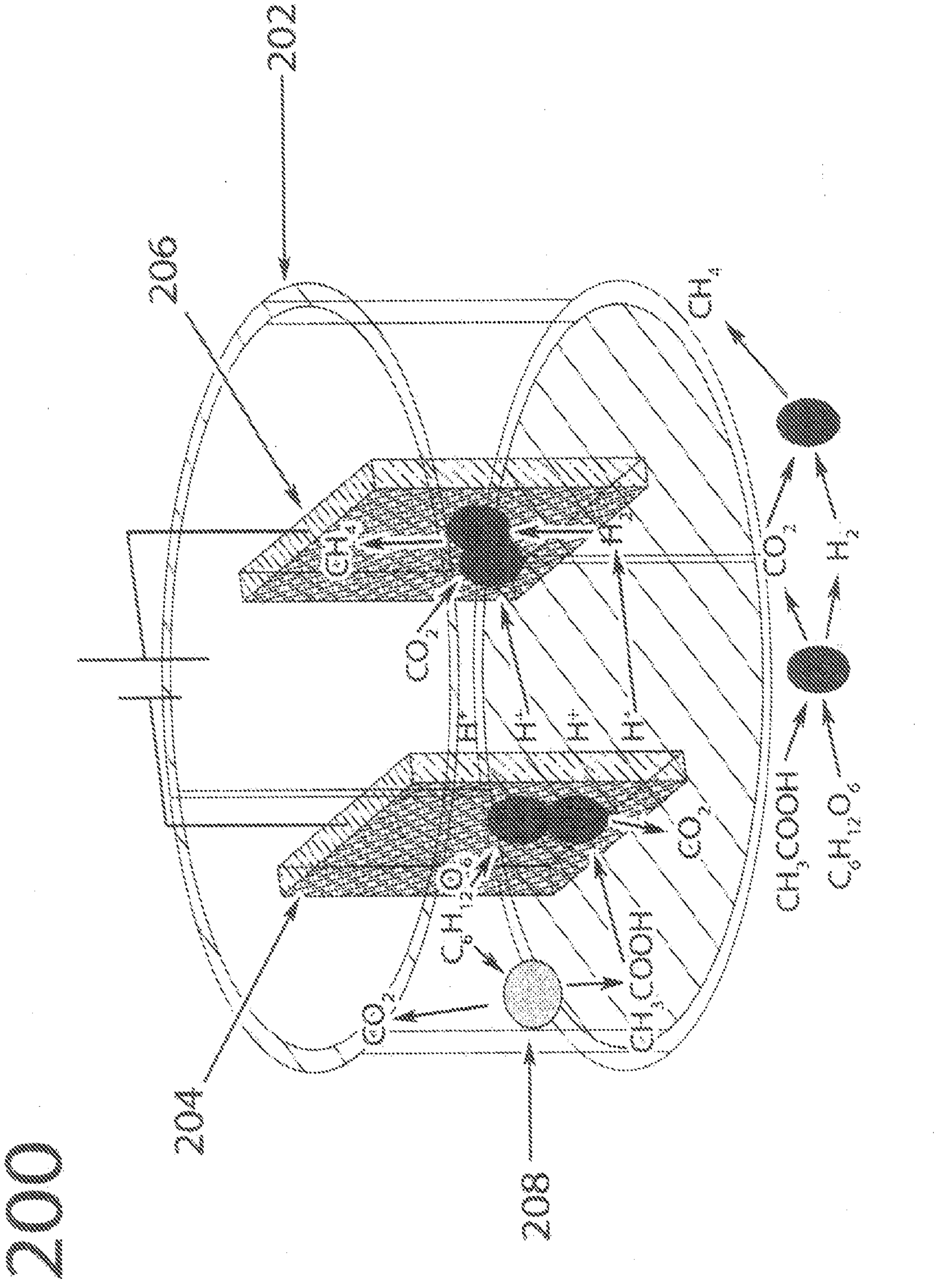
microbes
CO_2
H^+
anode
cathode
O_2
H_2O
H^+

FIG. 2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H$^+$
CO$_2$
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C$_6$H$_{12}$O$_6$
CO$_2$
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CH$_4$

FIG. 3

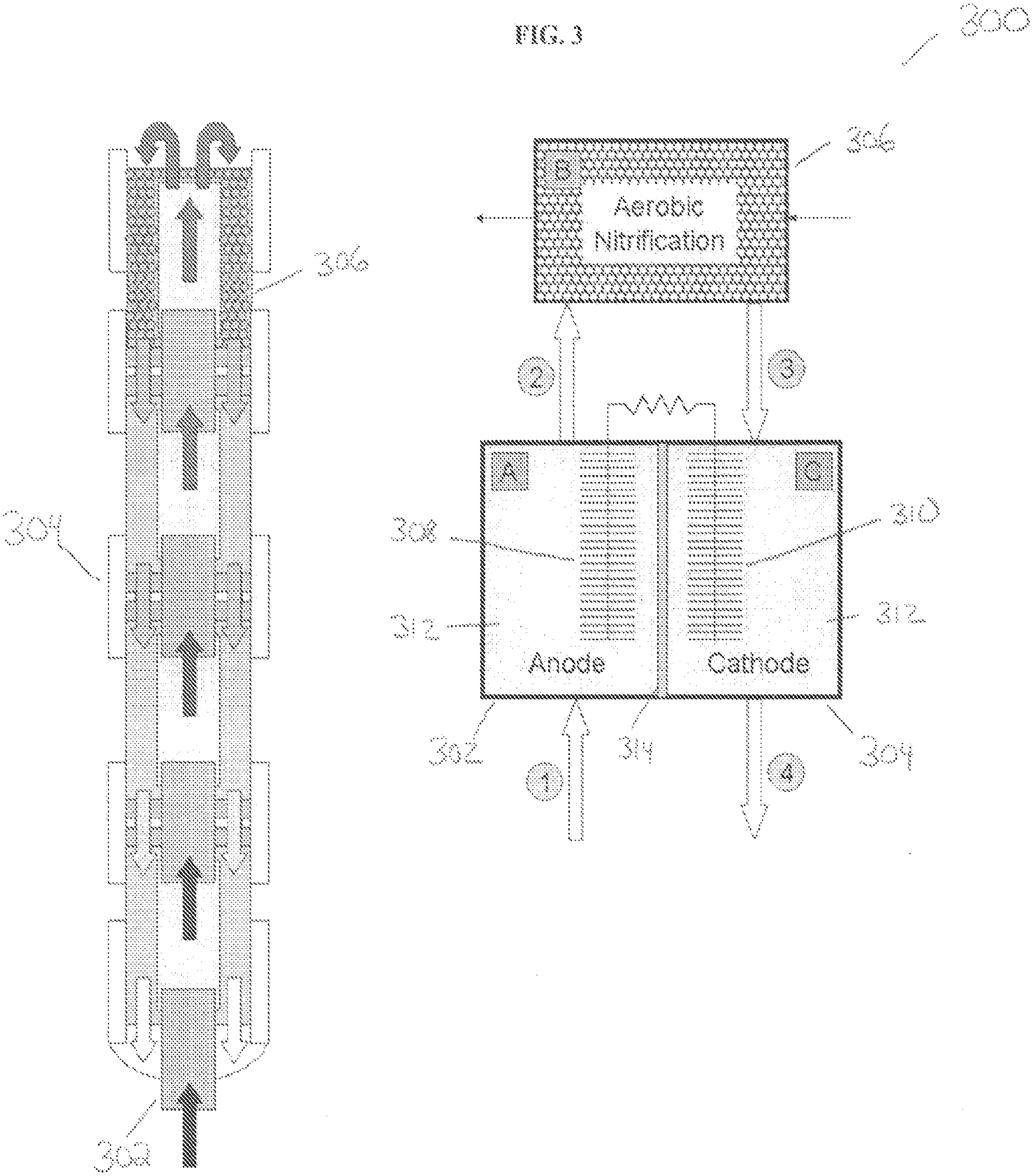

300
306
304
302
B
Aerobic Nitrification
2
3
A
C
308
310
312
312
Anode
Cathode
302
314
304
1
4

FIG. 4A

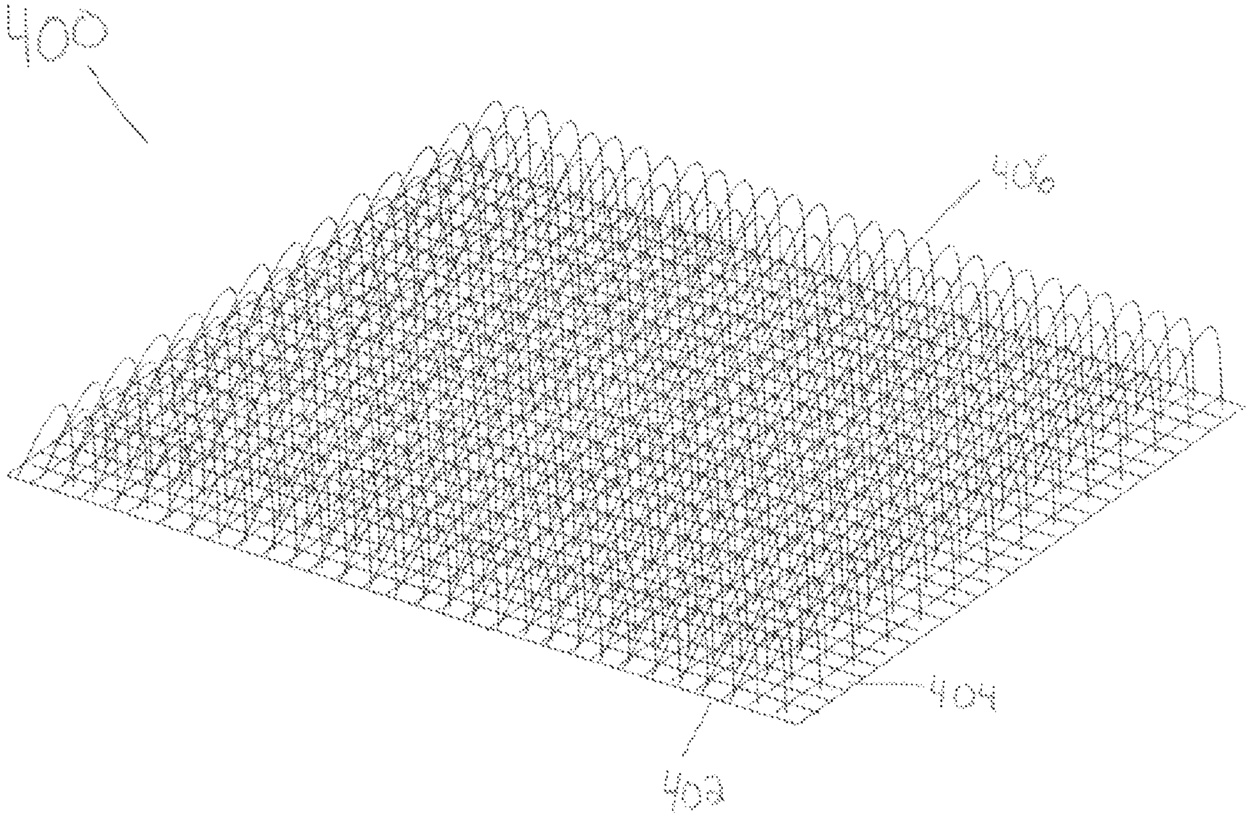


FIG. 4B

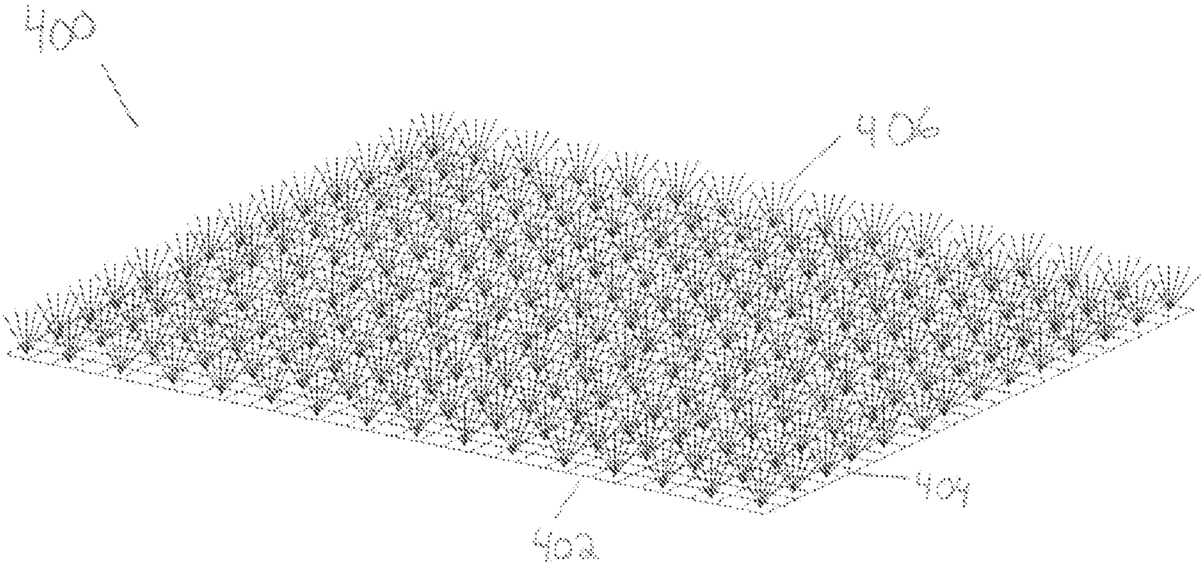


FIG. 5A

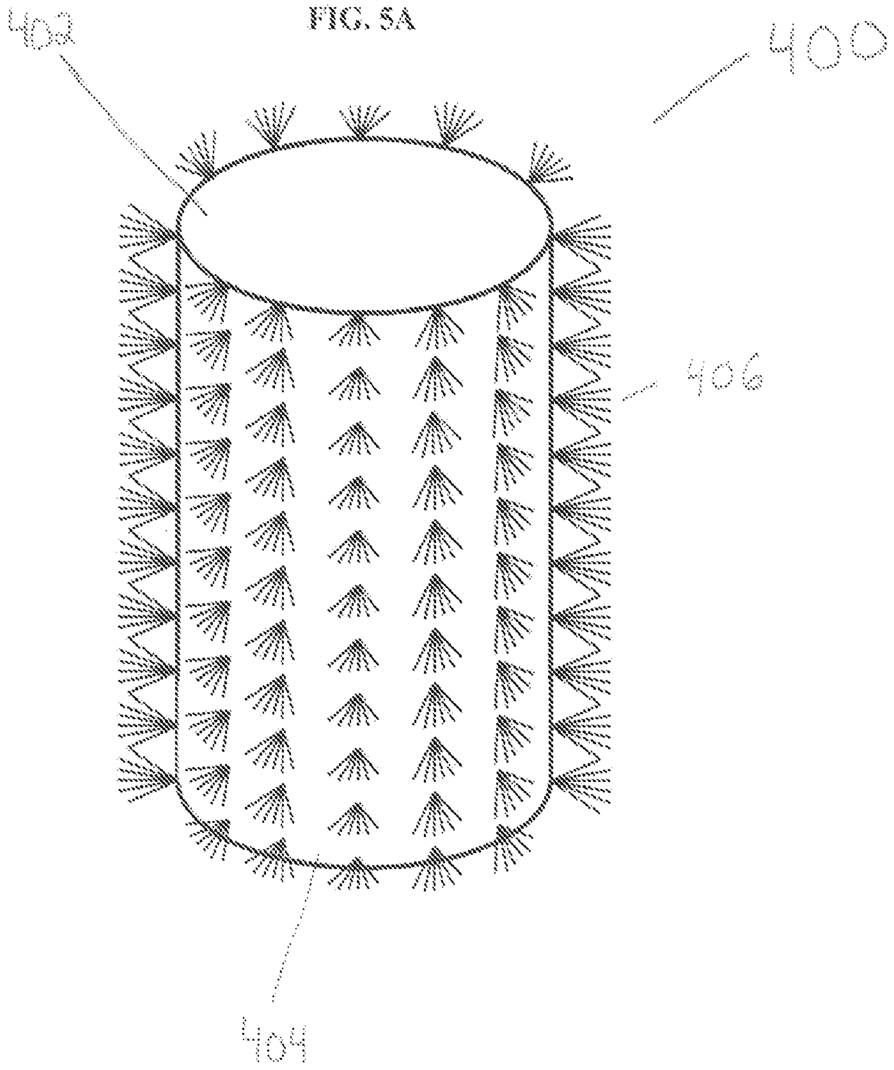


FIG. 5B

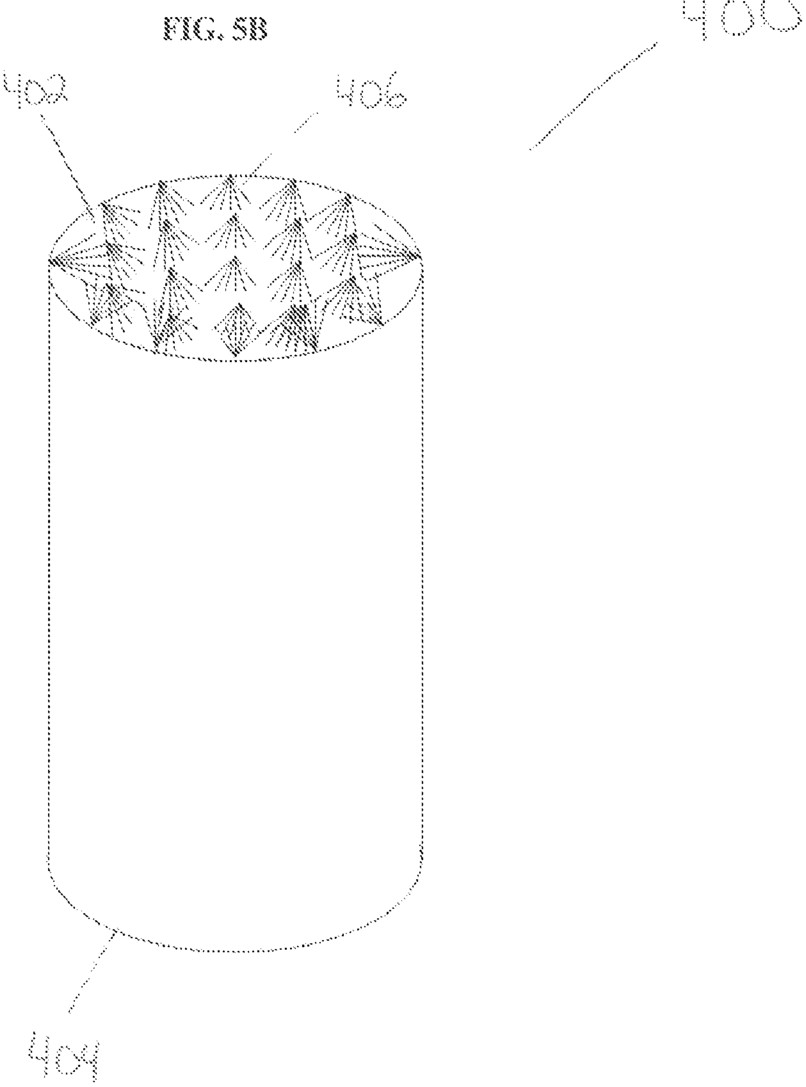


FIG. 6

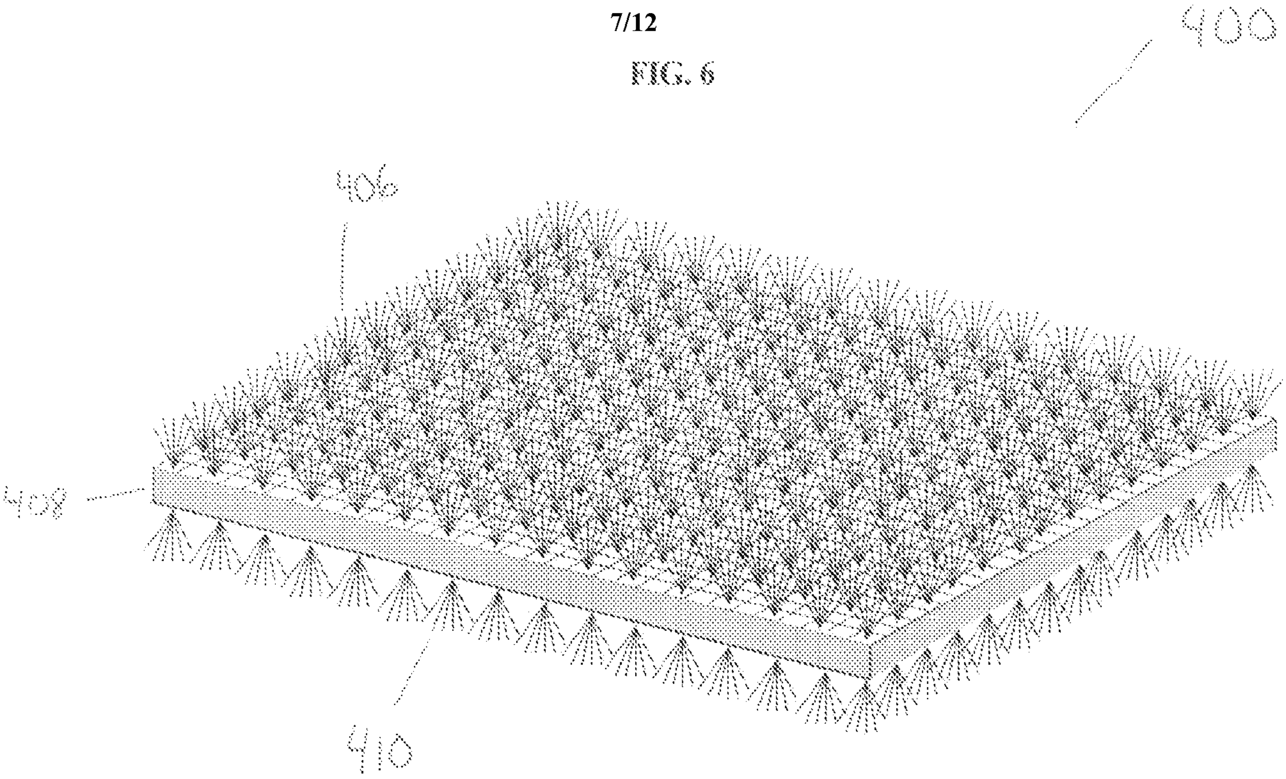


FIG. 7

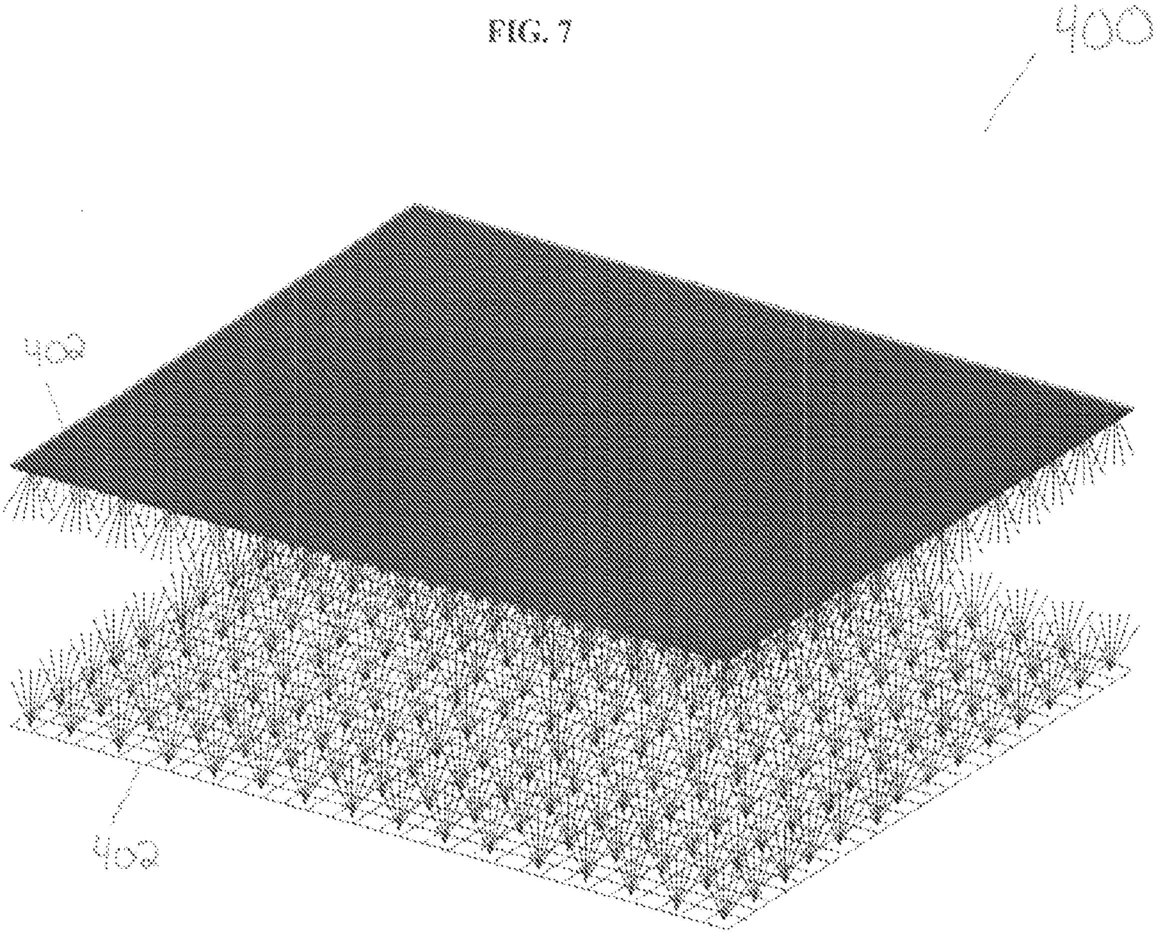


FIG. 8

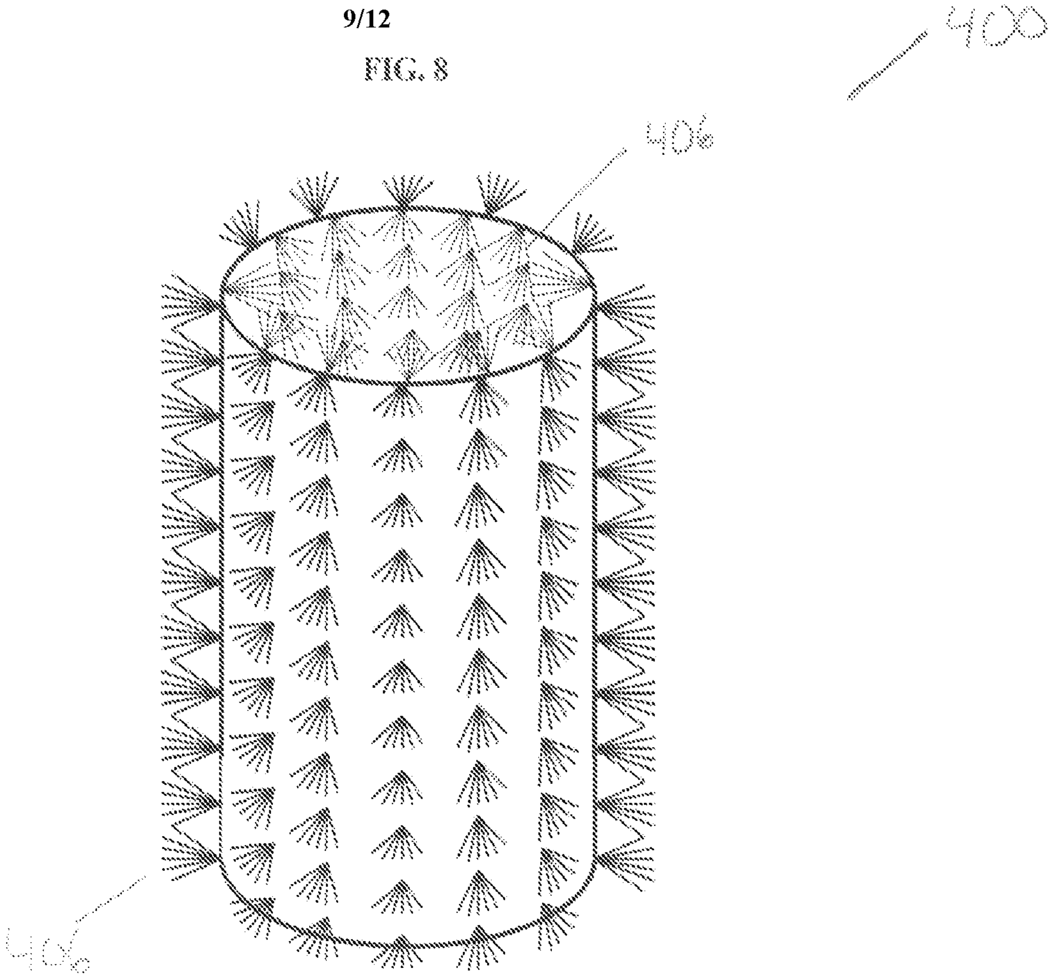


FIG. 9A

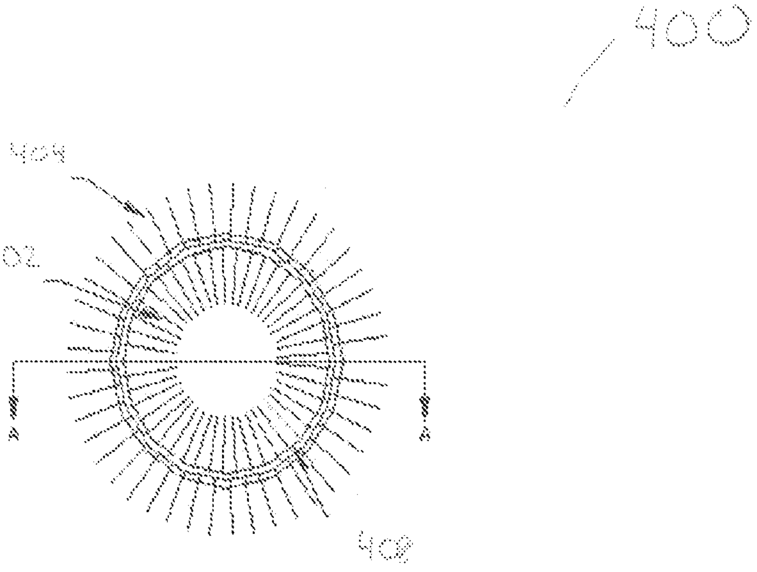


FIG. 9B

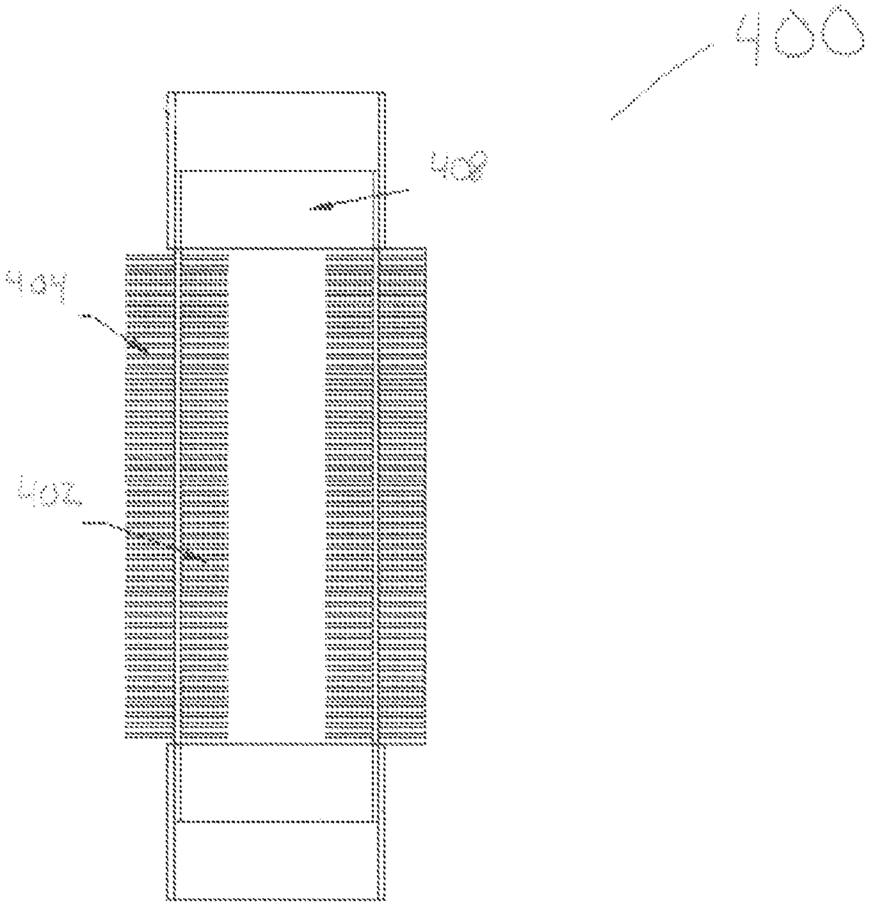
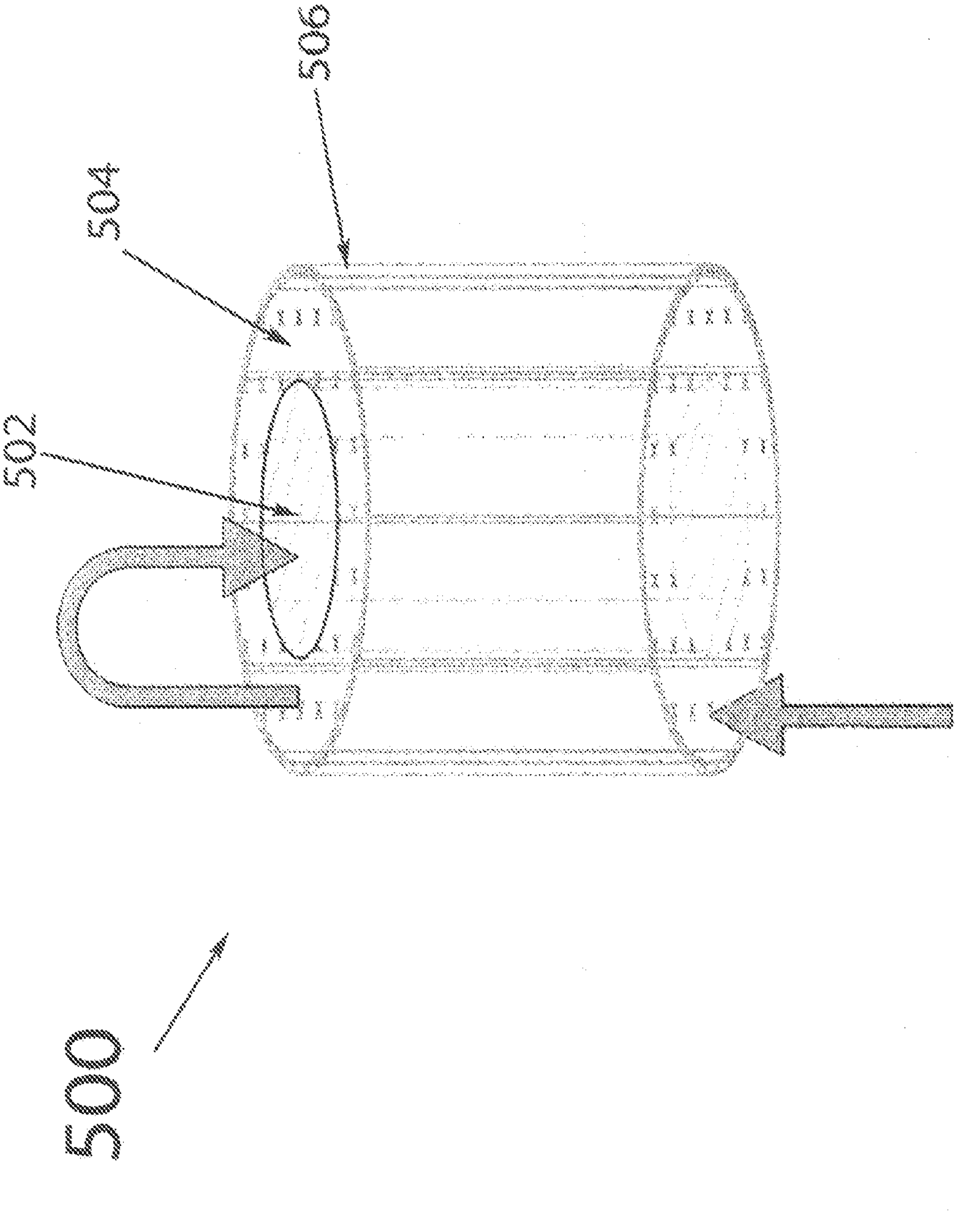


FIG. 10



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2010/025224

A. CLASSIFICATION OF SUBJECT MATTER

C02F 11/04(2006.01)i, C02F 1/46(2006.01)i, C02F 3/28(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)
C02F 11/04; H01G 9/058; H01M 8/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: bioelectrochemical, methagogenic, electrode, fuel cell

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008-059331 A2 (FEDOROVICH, VYACHESLAV VIKTOROVICH et al.) 22 May 2008 See abstract, page 9, line 34 - page 10, line 2, page 11, lines 20-32, claims 1, 24 and figure 1.	1-34
A	WO 2004-004036 A2 (NEDERLANDSE ORGANISATIE VOOR TOEGEPAST - NATUURWETENSCHAPPELIJK ONDERZOEK TNO et al.) 08 January 2004 See page 3, lines 20-24, page 9, lines 9-20, page 12, lines 7-23, claim 1 and figure 2.	1-34
A	JP 08-138978 A (JAPAN GORE TEX INC) 31 May 1996 See abstract, paragraphs [0006], [0008], claims 1, 2 and figure 1.	1-34
A	KorneelRabaey et al., "Microbial fuel cells: novel biotechnology for energy generation", TRENDS in Biotechnology Vol.23, No.6, pp.292-298 (2005)	1-34

☐ 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 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
11 OCTOBER 2010 (11.10.2010)

Date of mailing of the international search report
12 OCTOBER 2010 (12.10.2010)

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
Government Complex-Daejeon, 139 Seonsa-ro, Seo-gu, Daejeon 302-701, Republic of Korea
Facsimile No. 82-42-472-7140

Authorized officer
kang, Won Gil
Telephone No. 82-42-481-8711

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2010/025224

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