ELECTROLYTIC CELL AND METHOD OF USE THEREOF

Cross Reference to Related Applications

[0001] This application claims the benefit of U.S. Provisional Patent Application Nos. 61/153,253, filed February 17, 2009; 61/237,476, filed August 27, 2009; and 61/304,403, filed February 13, 2010, each of which is incorporated herein in its entirety by reference.

Background

[0002] Renewable resources for producing electricity are often intermittent. Solar energy is a daytime event and the daytime solar-energy-concentration potential varies seasonally. Wind energy is highly variable. Falling water varies seasonally and is subject to extended drought. Biomass is seasonally variant and subject to droughts. Dwellings have greatly varying demands including daily, seasonal, and occasional energy consumption rates. Throughout the world, energy that could be delivered by hydroelectric plants, wind farms, biomass conversion and solar collectors is neglected or wasted because of the lack of a practical way to save energy or electricity until it is needed. Demand by a growing world population for energy has grown to the point of requiring more oil and other fossil resources than can be produced. Cities suffer from smog and global climate changes caused by the combustion of fossil fuels.

[0003] Also, burgeoning demands have developed for hydrogen, oxygen, carbon, and other products that can be provided by thermochemistry or electrolytic dissociation of feedstocks such as water, biomass wastes, or organic acids derived from biowaste. For

example, the global market for hydrogen is more than $40 billion, and includes ammonia production, refineries, chemical manufacturing and food processing.

[0004] Electro-chemical production of fuels, metals, non-metals, and other valuable chemicals has been limited by expensive electricity, low electrolyzer efficiency, high maintenance costs, and cumbersome requirements for energy intensive operations such as compressive pumping of produced gases to desired transmission, storage, and application pressures. Efforts to provide technology for reducing these problems are noted and incorporated hereby in publications such as "Hydrogen Production From Water By Means of Chemical Cycles," by Glandt, Eduardo D., and Myers, Allan L., Department of Chemical and Biochemical Engineering, University of Pennsylvania, Philadelphia, PA 19174; Industrial Engineering Chemical Process Development, Vol. 15, No. 1, 1976; "Hydrogen As A Future Fuel, by Gregory, D.P., Institute of Gas Technology; and "Adsorption Science and Technology": Proceedings of the Second Pacific Basin Conference on Adsorption Science and Technology : Brisbane, Australia, 14-18 May 2000, By D. Do Duong, Duong D. Do, Contributor Duong D. Do, Published by World Scientific, 2000; ISBN 9810242638, 9789810242633.

[0005] Electrolyzers that allow hydrogen to mix with oxygen present the potential hazard of spontaneous fire or explosion. Efforts including low and high pressure electrolyzers that utilize expensive semi-permeable membrane separation of the gas production electrodes fail to provide cost-effective production of hydrogen and are prone to degradation and failure due to poisoning by impurities. Even in instances that membrane separation is utilized, the potential danger exists for membrane rupture and fire or explosion due to mixing of high-pressure oxygen and hydrogen.

[0006] Some commercial electrolyzers use expensive porous electrodes between which is an electrolytic proton exchange membrane (PEM) that only conducts hydrogen ions. (See Proton Energy Company and the Electrolyzer Company of Canada.) This limits the electrode efficiency because of polarization losses, gas accumulation, and reduction of available electrode area for the dissociation of water that can reach the interface of the electrodes and PEM electrolyte. Along with the limited electrode efficiency are other difficult problems including membrane ruptures due to the pressure difference between the oxygen and hydrogen outlets, membrane poisoning due to impurities in the make-up water, irreversible membrane degradation due to contaminants or slight overheating of the membrane, membrane degradation or rupture if the membrane is allowed to dry out while not in service, and degradation of electrodes at the membrane interface due to corrosion by one or more inducements such as concentration cell formation, galvanic cells between catalysts and bulk electrode material, and ground loops. Layering of electrode and PEM materials provide built in stagnation of the reactants or products of the reaction to cause inefficient operation. PEM electrochemical cells require expensive membrane material, surfactants, and catalysts. PEM cells are easily poisoned, overheated, flooded or dried out and pose operational hazards due to membrane leakage or rupture.

[0007] In addition to inefficiencies, problems with such systems include parasitic losses, expensive electrodes or catalysts and membranes, low energy conversion efficiency, expensive maintenance, and high operating costs. Compressors or more expensive membrane systems are situationally required to pressurize hydrogen and oxygen and other products of electrolysis. Corollaries of the last mentioned problem are unacceptable maintenance requirements, high repair expenses, and substantial decommissioning costs.

[0008] It is therefore an object of some embodiments of the present invention to provide an electrochemical or electrolytic cell, and a method of use thereof, for separated production of gases, including pressurized hydrogen and oxygen, that tolerates impurities and products of operation and address one or more of the problems with current methods set forth above.

Summary

[0009] In one embodiment of the present invention an electrolytic cell is provided comprising a containment vessel; a first electrode; a second electrode; a source of electrical current in electrical communication with the first electrode and the second electrode; an electrolyte in fluid communication with the first electrode and the second electrode; a gas, wherein the gas is formed during electrolysis at or near the first electrode; and a separator; wherein the separator includes an inclined surface to direct flow of the electrolyte and the gas due to a difference between density of the electrolyte and the combined density of the electrolyte and the gas such that the gas substantially flows in a direction distal to the second electrode.

[0010] In another embodiment, an electrolytic cell is provided comprising a containment vessel; a first electrode; a second electrode; a source of electrical current in electrical communication with the first electrode and the second electrode; an electrolyte in fluid communication with the first electrode and the second electrode; a gas, wherein the gas is formed during electrolysis at or near the first electrode; a gas extraction area; and a separator wherein separator comprises two inclined surfaces forming a "V" shape; wherein the separator directs flow of the electrolyte and the gas due to a difference between density of the electrolyte and the combined density of the electrolyte and the gas such that the gas substantially flows in a direction distal to the second electrode, and wherein the separator is

further configured to promote circulation of the electrolyte between the first electrode, the gas extraction area, and the second electrode to provide fresh electrolyte to the first electrode and the second electrode.

[0011] In yet another embodiment, an electrolytic cell is provided comprising a containment vessel; a first electrode; a second electrode; a source of electrical current in electrical communication with the first electrode and the second electrode; an electrolyte in fluid communication with the first electrode and the second electrode; a gas, wherein the gas is formed during electrolysis at or near the first electrode; and a separator; wherein the separator includes an inclined surface to direct flow of the electrolyte and the gas due to a difference between density of the electrolyte and the combined density of the electrolyte and the gas such that the gas substantially flows in a direction distal to the second electrode.

[0012] Other features and advantages of the present invention will become apparent from the following detailed description. It should be understood, however, that the detailed description and the specific examples, while indicating the preferred embodiments of the present invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the present invention will become apparent to those skilled in the art from this detailed description.

Brief Description of the Figures

[0013] **FIG 1** shows an electrolytic cell in accordance with an embodiment of the present invention.

[0014] **FIG 2** shows a magnified view of a portion of the embodiment of Figure 1.

[0015] **FIG 3** shows a variation of the embodiment of Figure 2.

[0016] **FIG 4** shows an electrolytic cell in accordance with an embodiment of the present invention.

[0017] **FIG 5** a magnified view of an alternative embodiment for a portion of electrolytic cell of Figure 4.

[0018] **FIG 6** shows a cross-section of a spiral electrode for use in a reversible fuel-cell.

[0019] **FIG 7** shows a system for converting organic feedstocks such as those produced by photosynthesis into methane, hydrogen, and or carbon dioxide.

Detailed Description

[0020] In order to fully understand the manner in which the above-recited details and other advantages and objects according to the invention are obtained, a more detailed description of the invention will be rendered by reference to specific embodiments thereof.

[0021] In one embodiment, an electrolytic cell and method of use is provided. While the electrolytic cell may be used in many applications, it is described in this embodiment for use in the production of hydrogen and oxygen. An electrolytic cell according to the present embodiment provides for reversible separated production of pressurized hydrogen and oxygen and tolerates impurities and products of operation. The embodiment further provides the option for operating an electrolysis process which comprises the steps of supplying a substance to be dissociated that is pressurized to a much lower magnitude than desired for compact storage, applying an electromotive force between electrodes to produce fluid products that have less density than the substance that is dissociated and restricting expansion of the less dense fluid products until the desired

pressure for compact storage is achieved. This and other embodiments can improve the energy utilization efficiency of dwellings such as homes, restaurants, hotels, hospitals, canneries, and other business facilities by operation of heat engines or fuel cells and to utilize heat from such sources to cook food, sterilize water and deliver heat to other substances, provide space heating or to facilitate anaerobic or electrically induced releases of fuel for such engines or fuel cells. Moreover, one skilled in the art will appreciate that aspects of the embodiments disclosed herein can apply to other types of electrochemical cells to provide similar advantages.

[0022] Contrary to conventional electrochemical electrodes which depend largely upon relatively slow diffusion, convection, and concentration gradient processes to produce mass transport and/or deliver ions for production of desired constituents, the present embodiment provides more efficient mass transport including rapid ion replenishment processes and deliveries to desired electrodes by pumping actions of low-density gases escaping from a denser liquid medium as described herein. This assures greater electrical efficiency, more rapid dissociation, and greater separation efficiency along with prevention of undesirable side reactions. Increasing the rate and efficiency of ion production and delivery to electrodes increases the system efficiency and current limit per electrode area.

[0023] Referring to Figure 1, an electrolytic cell 2 in which a container 4 such as a metallic tube serves as a containment vessel is shown. Optionally, the container 4 may also serve as an electrode as shown in Figure 1. A porous electrode such as cylindrical conductive wire screen electrode 8 is coaxially located and separated from tubular electrode 4 by an electrolytic inventory of liquid such as an acid or base. Liquid electrolyte occupies the interior space of container 4 to the liquid-gas interface in insulator 24. A layer of plated, plasma sprayed, or composited electrode material on a dielectric sleeve or a conductive

cylindrical inner liner electrode 4' (not shown) may be provided within container 4 to serve as an electrically separated element of the assembly to enable convenient replacement as a maintenance item or to serve as one of a number of segmented electrode elements for purposes of optional polarity, and/or in series, parallel, or series-parallel connections. In the present reversible embodiment for the electrolysis of water, electrode 8 may be considered the electron source or cathode such that hydrogen is produced at electrode 8, and electrode 4 may be considered the anode such that oxygen is produced at electrode 4. Container 4 may be capable of pressurization. Pressurization of the contents of container 4 is restrained by sealed caps 30 and 46. Support, electrical insulation, and stabilization of components including electrode 8, gas separator 10, and electrical connection 32 are provided by dielectric insulator bodies 20 and 24 as shown. Pressurization of the electrolytic cell 2 can be accomplished by self-pressurization due the production of gas(es) during electrolysis, by an external source such as a pump or by any combination thereof.

[0024] Separator 10 is configured to be liquid permeable but to substantially prevent gas flow or transport from the cathode side of the separator to the anode side of the separator and vice versa, include substantially preventing the flow of gas dissolved in the electrolyte or after nucleation of gas bubbles. Optionally, electrode 8 may be configured to act as separator 10 such that a distinct separator is not necessary. Alternatively, separator 10 may include the electrode 8 or electrode 8 may include separator 10. In addition, separator 10 may also include the anodic electrode 4 or anodic electrode 4 may include separator 10.

[0025] Insulator 24 is shaped as shown and as needed to separate, collect and/or extract gases produced by electrodes such as 4 and 8 including utilization in combination with separator 10. In the concentric cylindrical geometry shown, insulator 24 has a central conical cavity within which gases released on electrode 8 are collected. Concentrically

surrounding this central cavity is an annular zone that collects the gases released from the surfaces of electrode 4' or from the inside of container electrode 4.

[0026] Optionally, a catalytic filter 48 may be placed in the upper collection passage of 24 as shown. Oxygen that manages to reach catalytic filter 48 including travel by crossing separator 10 can be catalytically induced to form water by reacting with hydrogen, which may then return to the electrolyte. The vast excess of hydrogen can serve as a heat sink to prohibit the heat released by this catalytic reaction from affecting the electrolytic cell. Purified hydrogen is supplied at fitting 26 as shown. Similarly it may be preferred to provide a catalytic filter 49 in the upper region of the circumferential annulus that collects oxygen as shown, for converting any hydrogen that reaches the oxygen annulus into water. Oxygen is removed at fitting 22 as shown. Alternatively, the catalytic filters may be placed at, near or inside fittings 22 and 26.

[0027] In illustrative operation, if water is the substance to be dissociated into hydrogen and oxygen, a suitable electrolyte is prepared such as an aqueous solution of sodium bicarbonate, sodium caustic, potassium hydroxide, or sulfuric acid and is maintained at the desired level as shown by sensor 50 that detects the liquid presence and signals controller 52 to operate pump 40 to add water from a suitable source such as reservoir 42 as needed to produce or maintain the desired inventory or pressure. Controller 52 is thus responsive to temperature or pressure control sensor 58 which may be incorporated in an integrated unit with liquid level sensor 50 or, liquid inventory sensor 51 and control pumps 36 and 40 along with heat exchanger 56 which may include a circulation pump of a system such as a radiator or heater (not shown) to receive or deliver heat. Similarly, a heating or cooling fan maybe utilized in conjunction with such operations to enhance receipt or rejection of heat from sources associated with the electrolytic cell 2.

[0028] In some embodiments where the electrolytic cell 2 is to be applied cyclically, e.g., when surplus electricity is inexpensive and not otherwise demanded, electrolytic cell 2 can be operated with considerable variation of the water inventory. At times that surplus electricity is not available or it is turned off, hydrogen and oxygen supplies may be extracted from container 4 and the system is allowed to return to ambient pressure. Ambient pressure water can then be added to fully load the system, which can be provided to have a large annular volume around the circumference of insulator 24 as may be desired to facilitate such cyclic low-pressure filling and electrolysis operations to deliver hydrogen or oxygen at the desired high pressure needed for pressure or chemical energy to work conversions, compact storage, and provide rapid transfers to vehicles, tools, or appliance receivers.

[0029] Upon application of current and generation of voluminous gaseous supplies of hydrogen and oxygen from a much smaller inventory of liquid, the system may be pressurized as desired and remains pressurized until the inventory of water in solution is depleted to the point of detection by sensors 50 or 51 which enables controller 52 to either interrupt the electrolysis cycle or to add water by pressure pump 40 from reservoir 42 as shown. It may be preferable to add water across a valve such as check valve 44 as shown to allow multiple duties or maintenance on pump 40 as needed.

[0030] Referring to Figures 1, 2 and 3, Figure 2 shows one embodiment of the separator 10 of Figure 1 in which the separator includes two inclined surfaces 14 forming a "V" shape. If the electrolyte is water based, electrons are added to porous electrode 8 such as a woven wire cylinder through connection 32 and are removed from container 4 through electrical connection 6 to continuously convert hydrogen ions into hydrogen atoms and subsequently diatomic molecules that can nucleate to form bubbles on or near electrode 8.

Hydrogen and oxygen bubbles are typically much less dense than water based electrolytes and are buoyantly propelled upward. Oxygen bubbles are similarly propelled upward and separated from hydrogen by the geometry of coaxial separator 10 as shown in the magnified section view of Figure 2. The configuration shown in Figure 2 may be used in any application in which the flow of gas formed during operation of the electrolytic cell 2 is desirable. Further, said separator configuration may be employed in other configurations of electrochemical cells known in the art. Alternatively, if the materials formed during electrolysis is of a higher density than the electrolyte, separator 10 may be inverted forming a "Λ" shape. Similarly if one material formed at the cathode by electrolysis is less dense than the electrolyte and another material formed at the anode is more dense that the electrolyte, separator 10 may be comprised of a slanted "/" or "\" shapes to deflect the less dense material away from the more dense material.

[0031] Mixing of hydrogen with oxygen that is released from 4' or the inside of container 4 is prevented by a liquid-permeable barrier, separator 10 which efficiently separates gases by deflection from the surfaces 12' and 14 which are inclined against oxygen and hydrogen entry, flow, or transmission as shown. Alternatively, separator 10 may include a helical spiral that is composed of an electrically isolated conductor or from inert dielectric material such as 30% glass filled ethylene-chlorotrifluoroethylene in which the cross section of the spiraled strip material is in a "V" configuration as shown to serve as an electrical insulator and gas separator.

[0032] Passageways for fluid travel can be increased as desired to meet fluid circulation and distribution needs by corrugating the strip occasionally or continuously particularly at each edge to produce clearance between each layer of the helix, or alternatively at the stack of formed disks that make up the section shown in Figure 2 as a magnified

corrugations as shown at 13 in section view. It is generally advantageous to have each of such corrugations undulate about an appropriately inclined radial axis more or less as shown with respect to axis 15 and 15'. This allows the overall liquid-porous but gas-barrier wall thickness of separator 10 that is formed to be a desired thickness, for example, about 0.2 mm (0.008") thick or less.

[0033] Separator 10 may be of any suitable dimensions including very small dimensions and with respect to surface energy conditions sufficient to allow the liquid electrolyte to pass toward or away from electrode 8 while not allowing passage of gases because of the buoyant propulsion and upward travel of the gas. An alternative embodiment applicable in, for example, relatively small fuel cells and electrolyzers, is provided by a multitude of closely-spaced flattened threads with the cross section shown in Figure 2 in which such threads are woven or adhered to threads that provide mostly open access of liquids and are disposed in the mostly vertical direction on one or both sides of the "V" shaped threads. This allows the overall liquid-porous but gas-barrier wall thickness of separator 10 that is formed to be about 0.1 mm (0.004") thick or less.

[0034] Upward buoyant propulsion deflects gas bubble collisions on the inclined surfaces 12 and 14. This feature overcomes the difficulties and problems of the prior art conventional approaches that cause inefficiencies due to one or more of electrical resistance, fouling, stagnation, corrosion, and polarization losses. Moreover, some configurations can promote electrolyte circulation in concentric layers due to the buoyant pumping action of rising bubbles that produces flow of electrolyte upward and, as the gas(es) escape at the top of the liquid, the relatively gas-free and denser electrolyte flows toward the bottom as it is recycled to replace the less dense electrolyte mixed with bubbles or including dissolved gas. A heat exchanger 56 may be operated as needed to add or remove heat from electrolyte that is

circulated from the top of container 4 to the bottom as shown. Pump 36 may be used as needed to increase the rate of electrolyte circulation or in conjunction with pump 40 to add make up water.

[0035] In some embodiments high current densities are applied, including systems with rapid additions of organic material. In such embodiments, it may be advantageous to circulate the electrolyte with pump 36 which returns relatively gas free electrolyte through fitting 28 through line 34 to pump 36 to return to container 4 through line 38 and fitting 16 as shown. It may be preferred to enter returning electrolyte tangentially at fitting 16 to produce a swirling delivery that continues to swirl and thus synergistically enhances the separation including the action by separator 10 that may be utilized as described above. Depending upon the pressure of operation, hydrogen is about fourteen times less dense and more buoyant than the oxygen and tends to be readily directed at higher upward velocity by separator 10 for pressurized collection through filter 48 at fitting 26. At very high current densities and in instances that electrolytic cell 2 is subjected to tilting or G-forces as might be encountered in transportation applications, the velocity of electrolyte travel is increased by pump 36 to enhance swirl separation and thus prevents gases produced on an anode from mixing with gases produced by a cathode.

[0036] Some embodiments of non-conductive gas barrier and liquid transmitting embodiments including separator 10 enable much less expensive and far more rugged and efficient reversible electrolyzers to be manufactured than previous approaches including those that depend upon proton exchange membranes to separate gases such as hydrogen and oxygen. In one aspect, separator 10 can be designed to improve electrolyte flow during electrolysis. For example, separator 10 can be configured to promote the spiral flow of ions in liquid electrolyte inventories traveling upward from port 16 to port 28. This assures that

each portion of the electrodes receives freshly replenished ion densities as needed for maximum electrical efficiency. Such electrode washing action can also rapidly remove bubbles of hydrogen and oxygen as they form on the respective electrodes of the electrochemical cell.

[0037] Figure 3 shows the edge view of representative portions of component sheets or helical strips of another aspect of separator 10 for providing electrical isolation adjacent electrodes including flat plate and concentric electrode structures while achieving gas species separation as described above. In assembly 11, sheets 12' and 14' form a cross section that resembles and serves functionally as that of separator 10. Flat conductive or non-conductive polymer sheet 12' is prepared with multitudes of small holes on parallel centerlines that are inclined to form substantial angles such as shown by first angle 15 of approximately 35^{o} to 70^{o} angles with the long axis of sheet 12' as shown. Polymer sheet 14' is similarly prepared with multitudes of small holes on parallel centerlines that are substantially inclined as shown by second angle 15' to form approximately 35^{o} to 70^{o} angles with the long axis of sheet 14' as shown.

[0038] In other embodiments the angles 15 and 15' can be varied depending on the material to separated during the electrolysis process. For example the angles could be declined, for electrolysis of compounds that have no gaseous constituent or only one gaseous constituent. If a compound such as Al_2O_3 is dissociated by electrolysis in cryolite-alumina electrolyte to form aluminum and oxygen, the aluminum is more dense than the cryolite-alumina electrolyte and the aluminum separating cathode electrode or associated separator would be configured (by, e.g., declined angles) to send the aluminum downward and away from the oxygen traveling upward.

[0039] Multitudes of such small holes with diameters of about 1/12 to 1/3 of the sheet thickness dimension can readily be made in sheets 12' and 14' by suitable technologies including laser drilling, hot needle piercing, or by high-speed particle penetrations. Sheets 12' and 14' each of which are typically about 0.025 to 0.25 mm (.001" to 0.10") thick can be held together by welding or otherwise bonding, thread ties, elastic bands, or one or more spiral wraps of conductive or nonconductive wire on the resulting outside diameter to form as an assembly with electrode 8. Sheets 12' and 14' may also be joined occasionally or continuously by adhesives or by thermal or solvent fusion. Thus, where the inclined holes of sheet 12' overlap the holes of sheet 14' passageways are formed to enable liquid and/or electrolyte travel while prohibiting gas transmission through the gas barrier membrane that is formed. Referring to Figures 1 and 4, tubular constructions of the assembled gas barrier sheets may be formed with the appropriate diameter for embodiments 2 or 100 by adhering or welding the butt seam or by providing an overlapped seam that performs as the intended separation gas barrier.

[0040] For electrolysis of water, a variety of electrolytes are suitable. In one embodiment potassium hydroxide may be used with low carbon steel for the containment vessel 4. Extended life with increased corrosion resistance may be provided by nickel plating cylinder 4 or by utilization of a suitable stainless steel alloy. In other aspects, increased containment capacity can be provided by overwrapping cylinder 4 with high-strength reinforcement such as glass, ceramic, or carbon filaments or a combination thereof.

[0041] Depending upon the particular application and strength requirements it may be advantageous to use about 30% glass filled ethylene chlorotrifluoro-ethylene for insulating separators 20 and 24. Electrode 8 may be made of woven nickel or type 316 stainless steel

wires. Separator 10 may be made from about 30% glass filled ethylene-chlorotrifluro-ethylene strip.

[0042] In another embodiment, it is also intended to utilize controlled applications of electricity to produce methane or hydrogen separately or in preferred mixtures from organic electrolytes. In some aspects, the embodiment can operate in conjunction with the embodiments of copending patent application including Serial No. 09/969,860, which is incorporated herein by reference. Anaerobic digestion processes of organic materials that ordinarily produce methane can be controlled to produce an electrolyte that releases hydrogen at considerably lower voltage or by a reduced on-time of a pulse-width modulated duty cycle and resulting electricity expenditure than that required to dissociate water.

[0043] Acidity or pH of the organic solution that is produced by microbial digestion can be maintained by a natural bicarbonate buffered interaction. The bicarbonate buffer may be supplemented by co-production of carbon dioxide in the digestion process. The process may be generalized for various steps in anaerobic digestion processes of organic compounds by illustrative digestion of a simple carbohydrate or glucose that may have many competing and complementary process steps such as:

$$C_6H_{12}O_6 + (\text{Anaerobic Acid formers, Facultative bacteria}) \rightarrow CH_3COOH \quad \text{Equation 1}$$

$$CH_3COOH + NH_4HC_6O_3 \rightarrow CH_3COONH_4 + H_2O + CO_2 \quad \text{Equation 2}$$

$$3CH_3COONH_4 + 3H_2O\ (\text{Bacteria}) \rightarrow 3CH_4 + 3NH_4HCO_3 \quad \text{Equation 3}$$

[0044] In instances that methane from such solutions is desired, pH control near 7.0 may be needed. At ambient pressure, pH of about 7.0, and 35-37°C (99°F), methanogenesis is favored. Most domestic wastewater contains biowastes with both macro and micronutrients required by the organisms that provide methanogenesis. Maintaining relatively large concentrations of dissolved and distributed hydrogen or monosaccharides present in the anaerobic reactor may inhibit operations of methane-forming microorganisms.

[0045] In another aspect, increased production of fuel values from organic substances can be accomplished by application of an electric field to cause dissociation of substances such as acetic acid (CH_3COOH) that are produced by bacterial breakdown of glucose and other organic compounds and by other acid-production processes that yield hydrogen ions.

$$CH_3COOH \rightarrow CH_3COO^- + H^+ \qquad \text{Equation 4}$$

[0046] Hydrogen ions migrate or are delivered to the negatively charged electrode and gain electrons to produce hydrogen gas.

$$2H^+ + 2e^- \rightarrow H_2 \qquad \text{Equation 5}$$

[0047] Two electrons are supplied by the negatively charged electrode. At the other electrode the electrochemical reaction includes oxidation of the acetate ion to carbon dioxide and hydrogen ions as summarized in Equation 6.

$$CH_3COO^- + 2H_2O \rightarrow 2CO_2 + 7H^+ + \text{Electrons} \qquad \text{Equation 6}$$

[0048] In this electrode reaction, acetate ions lose electrons, subsequently react with the water and break up into carbon dioxide gas and hydrogen ions. Carbon dioxide saturates the solution and is released from the liquid solution interface as set forth in the above embodiments. Hydrogen ions are circulated and/or migrate until electrons are received from the opposite electrode to produce hydrogen atoms and then diatomic molecules as summarized in Equation 5 for separate co-collection in such systems. Separated collection is highly advantageous, for example, separated collection to cause pressurization or at high pressure as a result of liquid pumping instead of gas compression, is especially efficient and greatly reduces the capital equipment ordinarily required to separate and then mechanically compress the hydrogen , methane or carbon dioxide produced.

[0049] Decomposition by anaerobic digestion of compounds such as acetic acid to produce hydrogen and carbon dioxide requires much less energy than electrolysis of water, because, in part, the digestion reactions yield hydrogen ions and exothermic energy. Initialization and maintenance of the exothermic decomposition of acids such as acetic acid may be accomplished at lower voltage applications or by intermittent or occasional electrolysis instead of continuous electrolysis as typically required to decompose water. The free energy of formation of water at ambient temperature is quite large (at least 1KWH = 3,412 BTU of released hydrogen) compared to the electrolysis of digester substances and acids such as urea and acetic acid to hydrogen and carbon dioxide, which requires relatively minimal activation and/or catalytic action particularly by organic catalysts. Accordingly, selected catalysts including modifications to Raney-Nickel catalysts, nickel-tin-aluminum alloys, selections from the platinum metal group, platinum-nickel and other platinum-transition metal single crystal alloy surfaces, and various organic catalysts utilized in

conjunction with the electrode systems set forth herein further improve the rate and/or efficiency of hydrogen production.

[0050] In another aspect, it may be preferred to utilize numerous cells of electrode pairs connected in switchable series or parallel or series-parallel for purposes of matching the available source amperage and voltage with the voltage required for dissociation by series connection of cells such as shown in Figure 1. In one aspect of this embodiment, each cell may require about 0.2 to 2 volts depending upon the aqueous electrolyte chosen or biochemically produced from organic substances so a home-size 6-volt photovoltaic source could have 3 to 30 cells in series and an industrial 220-volt service may have about 100 to 1,000 electrode cells connected in series. Product gases could readily be delivered by parallel or series collection arrangements. Depending upon the desired flexibility for adjusting the number of series and/or parallel connections, support and flow control feature 18 may be by an insulating or non-insulating material selection.

[0051] At various current densities, including at medium and low current densities, it may be preferred to allow buoyant propulsion of the bubbles that are generated to accomplish circulation of the electrolyte to prevent ion depletion and stagnation problems. At start-up or higher current densities one can operate pump 36 and heat exchanger 56 to provide the desired operating temperature and presentation of ion-rich electrolyte at the electrode surfaces. This enables extremely high rates of energy conversion in which energy such as off-peak electricity available from solar, wind, falling water, or wave resources is utilized to quickly and efficiently produce high-pressure supplies of oxygen and hydrogen or hydrogen and carbon dioxide or hydrogen and methane along with carbon dioxide for separated storage and use.

[0052] In one aspect of this embodiment, the problem of regenerative braking of vehicles or power-plant spin-down in which sudden bursts of large amounts of energy must be quickly converted into chemical fuel potential is addressed. A conventional fuel cell for truck, bus, or train propulsion cannot tolerate high current densities that are suddenly applied to the fuel cell electrodes. This embodiment overcomes this limitation and provides extremely rugged tolerance of high current conditions while achieving high electrolysis efficiency without the problems of PEM degradation or electrode-interface failures that regenerative PEM fuel cells suffer. Because of the rugged construction and extremely ample opportunities for cooling that are provided, extremely high current operations are readily accommodated. Conversely, this embodiment readily starts up and operates efficiently in severe cold or hot conditions without regard for various PEM-related difficulties, limitations, and failures.

[0053] In another aspect, in order to achieve much higher return on investment in energy conversion systems such as a hydroelectric generating station, wind farm, system of wave generators, or conventional power plants, the embodiment allows off-peak electricity to be quickly and efficiently converted into hydrogen and oxygen by dissociation of water or hydrogen and carbon dioxide by dissociation of substances generated by anaerobic digestion or degradation of organic matter. A compact version of the embodiment can occupy a space no larger than a washing machine and convert off-peak electricity that might otherwise go to waste into enough hydrogen to operate two family size vehicles and provide the energy requirements of the home.

[0054] As set forth above, some embodiments provided herein provide more efficient mass transport including rapid ion replenishment processes and deliveries to desired electrodes by pumping actions of low-density gases escaping from denser liquid medium.

This assures greater electrical efficiency, more rapid dissociation, and greater separation efficiency along with prevention of undesirable side reactions. Increasing the rate and efficiency of ion production and delivery to electrodes increases the system efficiency and current limit per electrode area. Applications that convert organic substances into carbon dioxide and hydrogen or methane are particularly benefited by: enhanced rates of delivery of organic substances to microorganisms that participate in the process, incubation and delivery of incubated microorganisms to extend and self-repair biofilm media, more rapid separation of produced gases and delivery of organic substances along with more efficient delivery of intermediate ions to electrodes.

[0055] Referring to Figure 4, another embodiment, electrolytic cell 100 is shown that is particularly beneficial in applications in which it is not desired to apply voltage or to pass current through the inside walls of containment vessel 102. The embodiment also facilitates series connections of bipolar or multiple electrode sets or cells such as 110 and 114 within the electrolytic cell 100 to simplify gas collection and voltage matching needs.

[0056] In one aspect in which that containment vessel 102 is cylindrical and the components within are concentric, electrode assemblies 110 and 114 may be formed from numerous nested truncated conical components or one or both electrodes may be formed as a helical electrode as described above. Electrodes 110 and 114 may be of the same, similar or different configurations. In another aspect, electrode 114 may be assembled from nested truncated conical sections or it may be a spiral electrode that continuously encircles electrode 110.

[0057] Electrical separation of electrodes 110 and 114 to prevent short circuits may be accomplished by various means including by controlled tolerances for the operating

dimensions and/or by the use of dielectric threads or filaments placed between electrodes 110 and 114 and/or by another form of separator 10 or 111 as disclosed regarding Figures 2 and 5.

[0058] The electrolytic cell 100 may be pressurized. Pressure containment is provided by upper and lower caps 104 and 106 as shown. Insulators 120 and 122 are supported by caps 104 and 106 as shown. The circuit components and hardware for electrical and fluid connections are illustrative and can be accomplished by penetrations through caps 104 and 106 as needed to meet specific application needs.

[0059] In the current embodiment, both electrodes 110 and 114 are formed to have inclined surfaces that direct the substance produced such as gas released to respective collection zones as shown. Illustratively, if water is to be dissociated from a suitable electrolyte, electrode 110 may receive electrons that are supplied through connection 108, which is sealed in cap 106 by plug seal 132. Electrons are thus taken from electrode 114 through plug seal 130, which provides insulation of contact 124 as a gas such as carbon dioxide or oxygen is released on electrode 114.

[0060] Such gases are thus propelled by buoyant forces and travel more or less upward as delivered by electrode 114 and along the inside wall of container 102. Hydrogen is propelled upward as delivered by electrode 110 and within the center core formed by numerous turns or conical layers of electrode 110 and collected as shown at insulator 120. Purified hydrogen at design pressure is delivered by pressure fitting 116. Catalytic filter 134 may be used to convert any oxidant such as oxygen that reaches the central core to form water. A similar catalytic filter material may be used to produce water from any hydrogen that reaches the outer collection annulus in insulator 120 as shown. Pressurized filtered oxygen is delivered by pressure fitting 118.

[0061] Optionally, to improve the efficiency of the electrolytic cell 100, one or more gas collection vessels (not shown) may be in fluid communication with electrolytic cell 100 to collect gas formed during electrolysis. The gas collection vessel can be implemented to capture the gas at an elevated pressure prior to substantial expansion of the gas. The gas collection vessel can be further configured to capture work as the gas expands according to methods known in the art. Alternatively, the gas collection vessel can be configured to provide gas at pressure for storage, transport or use wherein the gas is desired to be delivered at an elevated pressure. It is further contemplated that said aspect can be implemented in various electrochemical cells.

[0062] Referring to Figure 2, in another aspect, a gas expander may be included at, near or inside fitting 22, fitting 26 or in a gas collection vessel in fluid communication with fitting 22 or fitting 26. Similarly, referring to Figure 4, a gas expander may be included at, near or inside fitting 116, 118 or in a gas collection vessel in fluid communication with fitting 116 or fitting 118.

[0063] In another aspect, a method and apparatus for electrolysis to pressurize a fluid coupled with a device to extract work from such pressurized fluid is provided. The fluid may be pressurized liquid, liquid-absorbed gas, vapor or gas. Conversion of pressurized fluid to vapor or gas may occur in or after fitting 116 and a device to convert the pressure and flow from such fittings could be selected from a group including a turbine, generator, vane motor, or various piston motors or an engine that breathes air and injects pressurized hydrogen from 116. Similarly conversion of pressurized fluid to vapor or gas could be in or after fitting 118 and a device to convert the pressure and flow from such fittings could be selected from a group including a turbine, generator, vane motor, or various piston motors or an engine that expands and/or combusts pressurized fluid such as oxygen from 118.

[0064] In another aspect, an apparatus and method to overcome the high cost and power losses of a transformer and rectifier circuit is provided. This is accomplished by adjusted matching of load voltage with source voltage by series connection of electrode cells or electrodes within a cell, such as connecting the negative polarity of a DC source to the lowest three turns of electrode 110 to the next three turns of electrode 114 to the next three turns of electrode 110 to the next three turns of electrode 114 and to the next three turns of electrode 110 et seq. and starting from the opposite (highest) end to connect the positive lead from the DC source to three turns of electrode 114 to the next three turns of electrode 110 to the next three turns of electrode 114 to the next three turns of electrode 110 to the next three turns of electrode 114 et seq. Turns and/or stacks of truncated cones may be adjusted to develop the area needed to match the source amperage.

[0065] In another aspect of this embodiment, in addition to providing separation of the gases produced by electrolysis, the pumping action developed by the invention provides for delivery of nutrients to microorganisms that, depending upon the relative scale of operations, are hosted in suitable media such as carbon cloth, activated carbon granules, expanded silica, graphite felt, coal, charcoal, fruit pits, wood chips, shredded paper, saw dust, and/or mixtures of such selections that are generally located within portions of electrode 110 and/or between portions of electrode 114 and container 102. Corresponding functions and benefits include thermal stabilization of the system, circulation of feedstocks and removal of products such as carbon dioxide and production of hydrogen from acids that may be produced by the incubation, nutrition, and growth of such microorganisms.

[0066] At low and medium current densities, buoyant forces induced by low density solutions and bubbles can circulate the electrolyte within container 102. At higher current densities it is advantageous to adaptively control temperature, pressure, and

circulation of the electrolyte as previously disclosed. External circulation of electrolyte may be from fitting 126 to fitting 138 as shown and includes situations in which one or numerous electrode cells connected in optional series and/or series-parallel circuits are contained within container 102.

[0067] In another aspect, the embodiment can be optimized for high current densities to deliver commensurately higher electrolyte fluid flow rates through one or more holes or grooves 139, which direct fluid at a tangent to the annular space between electrodes 110 and 114. Electrolyte flows upward along the helical spaces formed by the electrodes and is replenished by electrolyte entering helical paths provided by 110 and 114 from the annular space between 110 and 114. The angular momentum of the electrolyte entering the space between electrodes 110 and 114 increases the impetus of bubble lift pumping by electrolytic products such as hydrogen and oxygen respectively produced on electrodes 110 and 114 and adds to such momentum.

[0068] This circulation of electrolyte is highly beneficial for purposes of assuring rapid replacement of ions that become hydrogen and oxygen atoms or other gases such as carbon dioxide upon charge exchanges to and from electrodes 110 and 114 and for removing such gases for collection and removal with minimum electrical polarization loss during electrolysis. Thus very high current densities are readily accepted to efficiently electrolyze the circulated fluid. In another aspect, further accommodation of high current densities is provided by the vast cooling capacity of the design resulting from improved electrolyte circulation, which prevents harmful stagnation of products of electrolysis and/or phase changes such as steam nucleation, and reduction of effective electrode areas.

[0069] In another aspect, electrodes 110 and 114 may constitute spring forms that can be advantageously operated at a resonant frequency or perturbed by various inducements including piezoelectric drivers, rotating eccentrics, and the action of bubble formation and the acceleration thrust by less-dense mixtures of electrolyte and bubbles as higher density electrolyte inventories are delivered to the surfaces of electrodes 110 and 114 by the pumping action that results. In response to perturbation, electrodes 110 and 114 vibrate at natural or induced frequencies to further enhance dislodgement of bubbles from surfaces including nucleation sites and thus enable higher current densities and greater energy-conversion efficiency.

[0070] Induced vibration of helical spring-form electrodes such as 110 and 114 can also cause peristaltic mechanical action to enhance bubble acceleration toward the respective collection paths and exit ports of electrolytic cell 100. During this vibration, cyclic increases and decreases of the average distance and angle between adjacent layers of electrode turns produce fixed or traveling nodes depending upon the magnitude and frequency of the inducement(s).

[0071] Figure 5 shows a representative section view of a set of electrodes 110' and 114' for operation in conjunction with an electrically insulative spacer 111 between 110' and 114' including selections such as insulator 10 shown in Figure 2 that includes a helical flow delivery configuration for various applications or electrolytes. The assembly of concentric electrode 110', spacer 111, and electrode 114' provides a very rugged, self-reinforcing system for enabling efficient dissociation of fluids such as water, liquors from anaerobic digesters, or seawater with improved efficiency and resistance to fouling. Electrodes 110' and 114' may be constructed from conductive carbon papers, cloth, or felt; woven or felt carbon and metal filaments, graphite granules sandwiched between woven carbon or metal

filaments; or metal-plated polymers or metallic sheet stocks such as mild steel, nickel plated steel, or stainless steel that are drilled more or less as previously disclosed with multitudes of holes on parallel centerlines that are inclined as shown for respective separations of hydrogen from co-produced gases such as oxygen, chlorine, or carbon dioxide depending upon the chemical make up of the electrolyte.

[0072] In instances that electrode 110', spacer 111, and electrode 114' are utilized in concentric electrode deployments such as shown in Figure 4, hydrogen is delivered to port 116 and depending upon the substance undergoing dissociation, products such as oxygen, chlorine or carbon dioxide delivery is provided at port 118. In some instances it is preferred to provide the multitude of holes in 110' and 114' such that each hole is slightly tapered from the hole diameter on surface contacting spacer 111 to a larger diameter at the exit surface away from spacer 111.

[0073] It is preferred to select the helical pitch, width between electrodes, and thickness of the strip comprising spacer 111 for delivery of electrolyte from 138 to and through electrodes 110' and 114' to fitting 126 at rates that are commensurate with the electrical power available and the system heat transfer requirements to optimize the resulting width space between electrodes. This results in abundant deliveries of ions for electrolysis processes at electrodes 110' and 114' while assuring separation of hydrogen to the zone within electrode 110' and delivery of co-produced gases such as oxygen, carbon dioxide, or chlorine to the space outside of electrode 114'.

[0074] In another aspect, it is possible to operate the system regeneratively by providing gas flow grooves in the hydrogen electrode and gas flow grooves in the oxygen electrode along with appropriate fittings for adding hydrogen to the bottom of the hydrogen

electrode and oxygen at the bottom of the oxygen electrode. In this case it may be advantageous to utilize concentric spiral electrodes particularly in small fuel cells where a single canister assembly meets energy needs.

[0075] Referring to Figure 6, a cross-section of a spiral electrode(s) for use in instances that reversible fuel-cell operation is shown. This provides improvement of the surface to volume ratio, section modulus, and column stability of electrode 114 or of a similar helical version of electrode 110. Electrode 114 is illustrated in the section with gas 152 flowing along spiral grooves formed by corrugating the strip stock that is used to form the spiral and provide delivery of oxygen for fuel-cell operation and in electrolysis operation to deliver oxygen to annulus 136 and fitting 118. The same configuration works well for electrode 110 in fuel-cell and electrolysis modes for conversion of organic acids into carbon dioxide and hydrogen and in the electrolysis mode and assures plentiful gas delivery to the desired collection or source ports as previously described.

[0076] In another aspect, improved electrode performance is provided by facilitating the growth and maintenance of microorganisms that convert aqueous derivatives of organic substances such as carbonic, acetic, butyric and lactic acids along with compounds such as urea into hydrogen. On the electrode chosen for production of hydrogen ions and/or the release of carbon dioxide, increased microbe productivity is facilitated by preparing such electrode surfaces with topographical enhancements that increase the effective surface area including high aspect ratio filaments or whiskers that reduce electrical resistance to the substrate electrode and help hold microbes and biofilm in place along with the desired film substances provided by digestive processes.

[0077] Without being limited by theory, it is believed that the specific features of the electrode and/or separator, such as the topographical treatments or enhancement, promote turbulence, including cavitation or super cavitation, of the electrolyte at a desired location which in turn promotes nucleation at the location. Conversely, the specific configuration of the electrode and/or separator can inhibit turbulence, including cavitation or super cavitation at a desired location, for example, the point of electron transfer, which in turn inhibits nucleation at that location. It is contemplated that elements including these features can be implemented at any location in the electrolytic cell at which nucleation is desired. Moreover these same features and principles can be applied to a gas collection vessel or similar in fluid communication with the electrolytic cell, or to fluid communication with passages or valves there between.

[0078] Suitable filaments and or whiskers include metals or doped semiconductors such as carbon, silicon or nano-diameter filaments of carbon or boron nitride to provide increased surface area, reduce ion-transport and ohmic loses, increased microbe productivity and more effective nucleation activation for more efficient carbon dioxide release. Such filaments may also be utilized to anchor graphite granules that further improve microbe productivity, enhanced efficiency of enzyme and catalyst utilization, and related beneficial hydrogen ion production processes. Similarly, at the electrode where hydrogen ions are provided with electrons to produce hydrogen atoms and nucleate bubbles of diatomic hydrogen, filaments and whiskers may be utilized to increase the active area and reduce the voltage required for the overall process.

[0079] In addition to carbon whiskers, filaments grown from metals such as tin, zinc, nickel, and refractory metals deposited from vapor or grown from plating on suitable substrates such as iron alloy electrodes, have been found to provide reduced electrical

resistance and improved process efficiency. Such filaments or whiskers may be made more suitable for biofilm support and process enhancement by addition of conducive surfactants and or surface plating with suitable substances such as carbon, boron nitride, or silicon carbide deposited by sputtering or from decomposition of a substance such as a carbon donor from illustrative precursors such as acetylene, benzene, or paraffinic gases including methane, ethane, propane, and butane.

[0080] The embodiment of Figure 4 and variation thereof can provide advantageous separation of low density gaseous derivatives of fluid dissociation including hydrogen separation from organic liquors as summarized in Equations 1-6 to deliver hydrogen or selections of hydrogen-enriched mixtures to port 116 while carbon dioxide or carbon dioxide enriched mixtures including fixed nitrogen components are delivered to port 118. In some applications it may be desirable to reverse the polarity of these electrodes to reverse the delivery ports for gases that are separated. Such reversals may be long term or intermittent to accomplish various purposes. Depending upon selections of helical pitch(es) of electrodes 110 and 114 and each electrode's resonant or imposed frequency of vibration, and the relative fluid velocity at each electrode, hydrogen may be delivered to port 116 but the system may be operated to include methane and carbon dioxide. However, carbon dioxide delivered to port 118 may include methane and other gases of greater density than hydrogen. In applications that it is desired to provide Hy-Boost mixtures of hydrogen and methane to enable unthrottled operation of internal combustion engines, various burners, furnaces or fuel cells, the embodiment of Figure 4 operating with hydraulic and electrical circuit control provisions such as provided by pump 36 and controller 52, facilitates the option of producing and separating desired fuel mixtures with controlled ratios of hydrogen and methane for delivery at port 116.

[0081] An unexpected but particularly beneficial arrangement for production of vigorous anaerobic colonies of microbes that produce the desired conversion of organic feedstocks to hydrogen and/or methane is provided by adding media such as colloidal carbon, carbon filaments including nanostructures, exfoliated carbon crystals, graphene platelets, activated carbon, zeolites, ceramics and or boron nitride granules to the electrochemical cell. Such media may be doped or compounded with various agents to provide enhanced catalytic productivity. Illustratively, desirable functionality may be provided by doping with selected agents having electron structures more or less like boron, nitrogen, manganese, sulfur, arsenic, selenium, silicon, tellurium, and or phosphorous. Circulation induced by the gases released by the electrolysis process can promote sorting of such media into advantageous locations and densities for more efficient charge current utilization.

[0082] Without being limited to a particular theory, it is hypothesized that such synergistic results relate to increased surface areas in critical locations and development of stringers, regions, or filaments that enhance nucleation processes and or conduct electrons or hydrogen ions along with advantageous adsorption of enzymes, hydrogen, methane or carbon dioxide in biofilms and reaction zones that result. It is also indicated that microbes are incubated for circulation to efficiently utilized locations in the operations performed and flow paths produced in various embodiments disclosed herein.

[0083] In addition to whiskers and filaments such as carbon, graphite, various metal carbides, and silicon carbide and other inorganic substances and particles that catalytically enhance performance, it is beneficial to utilize activated substances and particles that present desired nutrients or catalysts to assist microbial processes. Illustratively, porous and/or exfoliated substrates of polymers, ceramics or activated carbon may adsorb conductive organic catalysts such as co-tetramethoxyphenylporphirine (CoTMPP) or poly(3,4-

ethylenedioxythiophene) (PEDOT) and or favorably orient and present other catalytic substances including enzymes and graft polymers that may also be utilized to incorporate and present catalytic substances including additional enzymes.

[0084] Suitable substances or graft polymers may include those of conventional, dendrimers, fiberforms, and other organic functional materials to minimize or replace platinum and other expensive catalysts and conductors. Such replacement substances and their utilization includes mixtures or staged locations with respect to the fluid circulation resulting from some embodiments disclosed herein. Variously specialized conductive and or catalytic structures include acicular deposits and fibers that may be grown or attached to the electrodes 4, 8, 110, or 114 and/or to overlaid carbon felts or woven structures or dispersed into developing biofilms. Illustratively, conductive and/or catalytic functionalities may be provided by filaments that retain and present hydrogenase and other enzymes, CoTMPP and or other catalysts such as poly (3, 4-ethylenedioxythiophene) (PEDOT) as fibers that are synthesized from aqueous surfactant solutions as self-organized thin-diameter, nanofibers with an aspect ratio of more than 100 and provide low resistance to charge conductivity. Synthesis in aqueous solutions including anionic surfactant sodium dodecyl sulfate (SDS) can be adapted to produce various configurations by changing the concentrations of SDS and furthermore by adding $FeCl_3$ to produce polymerized structures. (An exemplary procedure is described in Moon Gyu Han et al., Facile Synthesis of Poly (3, 4-ethylenedioxythiophene) (PEDOT) Nanofibers from an Aqueous Surfactant Solution, Small 2, No. 10, 1164-69 (2006), incorporated herein by reference.) Other examples include functional catalysts and micro-conductors in the form of nanocomposites derived from cellulose nanofibers and semiconducting conjugated polymers including polyaniline (PANI) and a poly(*p*-phenylene ethynylene) (PPE) derivative with quaternary ammonium side chains. Cellulose, carbon, or

ceramic whiskers with anionic surface charges can be combined with positively charged conjugated polymers to form stable dispersions that can be solution cast from polar solvents such as formic acid.

[0085] Preparations include graft polymers and end caps of organometallic alkoxides, metal alkyls and application of the catalytic benefits of acetic acid and a polymeric catalyst containing COOH end group. Special function and bifunctional end groups along with mixtures of end groups may be chosen to produce multi-functional characteristics including catalytic functions, reactive stabilizers, grafting agents, and promoters of dispersion polymerization. Similarly, specialized activation of carbon or other substrates by hydrogen and or enzymes produced by anaerobic microorganisms provides a locally hydrogen-rich environment to enhance or depress methane production and enhance additional hydrogen production from various organic substances.

[0086] Referring to Figures 1-3, optionally it may be advantageous to provide one or more supplemental felts and or woven screens of carbon filaments to the outside and inside surfaces of cylindrical components 8, 10, 11, 110, and or 114. Such supplemental felts and or woven screens may commensurately collect or distribute electrons in conjunction with electrodes 4, 8, 110, and or 114 and or separators 10 or 11 and help anchor or preferentially locate granules, filaments, and or other structures to reduce pressure losses or more equally distribute liquor flows and facilitate microbial functions in the desired energy conversion operations.

[0087] Among the complementary and competing reactions and processes to provide net production of hydrogen and carbon dioxide are various steps of processes summarized in Equation 8.

$$\text{Carbon} + 2H_2O \rightarrow CO_2 + 4H^+ + 4\ \text{Electrons} \qquad \text{Equation 8}$$

[0088] Carbon is consumed as summarized in Equation 8 including carbon that may be supplied as a constituent or a carbonaceous substance mixed with liquor from an anaerobic digester or electrolyzer or as a result of various manufacturing outcomes. Illustratively, carbon may include scrap from grinding, machining, electro-discharge-machining (EDM), and various thermochemical operations to produce electrodes, electrode coatings on electrodes including tank liners, or particles, or filaments, or flocculants, or selected carbides by thermal dissociation and reaction processes, including colloidal or other suspensions as an outcome of various degrees of dehydrogenization of organic substances.

[0089] Such carbon and/or carbon-donor feedstocks may be renewably supplied by bacteria, phytoplankton, or larger algae that receive carbon dioxide and other nutrients from the liquor supplied or by circulation of carbon dioxide to hydroponic and or soil-supported plants. It is advantageous to utilize such forms of carbon with high surface to volume ratios and to provide a voltage gradient to zones where they are delivered for the purpose of driving the reaction indicated and for delivering hydrogen ions to electrode surfaces including complementary conductive media such as filaments and conductive filter substances for production, nucleation, and release of hydrogen bubbles to increase the overall rate of hydrogen production.

[0090] Suitable provisions for increasing active surfaces and or flocculants include those with organic constituents such as bacteria, proteins, simple and complex sugars, cellulose, thermally dissociated cellulose, live and dissociated phytoplankton along with various forms of colloidal carbons, activated carbons, and carbides. Illustratively, phytoplankton and or larger algae may be grown, dried, mixed with a binder such as corn

syrup, thermally dehydrogenated to various extents and milled to provide finely divided flocculants. Alternatively, activated carbon feedstocks may be milled to provide finely divided particles that are utilized as enzyme receivers or flocculent media or it may be used in conjunction with the previously disclosed substances to enhance the desired production or efficiency of enzymes, to support incubation of desired microorganisms, or to increase hydrogen or methane production and or consumption of carbon to produce hydrogen ions for electrolysis as indicated by Equation 8.

[0091] If needed, occasional use of salt water or additions of small amounts of salt to water-based electrolytes can produce chlorine to quickly disinfect or to prevent harmful fouling of the electrolyzer systems shown. Utilization of some embodiments, for example Figure 5, enables the resulting system to be inherently free of harmful fouling even when utilizing electrolytes such as wastewater, commercial process water, wood-ash water, sea water, fly-ash water, canal and ditch water, or anaerobic digester liquor. Further, such systems can be quickly cleaned if needed by backflow of electrolyte or cleaning water from fitting 118 to 138 to dislodge particles that may have been delivered to the electrodes.

[0092] Applications of some embodiments include large community waste disposal operations to nano-size electrolyzers, include improvements to conventional waste digesters from which solutions or "liquor" containing organic substances is supplied for production of hydrogen and/or methane and or carbon dioxide and other plant nutrients. In this capacity some embodiments can provide rapid and efficient conversion of byproducts produced by anaerobic digesters and convert hydrogen ions into hydrogen and overcome acid degradation of the methane production operations. In operation, liquor from an anaerobic digester is utilized to produce hydrogen and carbon dioxide to provide beneficial restoration and or maintenance of pH near 7.0 instead of more acidic conditions that may stymie methane

production systems. This enables increased overall energy conversion efficiency as it overcomes the requirement for expensive provisions for addition of chemical agents to adjust the pH in digesters. In such medium and large applications it is beneficial to design and engineer multifunctional components including electron distribution circuits that may also provide desired retention of granules such as carbon, boron nitride, zeolites, polymers, and ceramics including such substances in variously activated conditions for enhanced performance.

[0093] In another aspect, an electrolyzer such as disclosed herein may be applied to provide rapid conversion of acids that are typically produced by anaerobic digestion including applications with municipal waste water and landfills along with wastes form slaughter houses, dairies, egg farms, and other animal feeding centers or similar. Production of methane is slowed or inhibited if acids that are produced by anaerobic conditions cause the pH to fall much below 7. Such acids can form if the feed rate of organic material exceeds the capacity of the methanogenic colony of microorganisms. By extracting hydrogen from such acids the rate of organic material processing by anaerobic digestion can be increased. The combination of methane and hydrogen provides much greater net energy production per ton of wastes, and the wastes are processed faster to increase the capacity of the process.

[0094] A particularly useful embodiment of the some embodiments is in waste-to-energy applications that utilize organic substances such as sewage along with hydrolyzed garbage, farm wastes, and forest slash in the anaerobic electro-digestion process summarized in Equations 1-6 to produce hydrogen with minimal or no oxygen production. The rugged configuration and recirculation operations enable great tolerance for dissolved solids including organic solids and particles in anaerobic process liquors that are utilized as electrolytes. Production of hydrogen without commensurate release of oxygen as would be

released by electrolysis of water facilitates higher efficiency and safety for utilization of the waste-sourced hydrogen as a cooling gas in electrical equipment such as an electricity generator.

[0095] In another application of some embodiments disclosed herein, electrolyzer system 900 as shown in Figure 7 provides for tissue and/or cellular disruption of biomass by enzyme, mechanical, thermal, acoustic, electrical, pressure and/or chemical actions and processes in conditioner 950 to enable faster or more complete processing, digestion and/or support of incubator purposes. Fluid including such disrupted cells from conditioner 950 and related feedstocks that are produced by converter 902 is circulated to electrolyzer 914 through annular distributor 922 of base 910 as shown. Anaerobic microorganisms are supported by media 940 and 942 and receive liquid recirculated from hydrogen separator 904 through conduit 910 and liquid recirculated from carbon dioxide separator 906 through conduit 908 as shown. Electrode 918 and/or media 942 releases hydrogen and electrode 916 and/or media 940 releases carbon dioxide. Electromotive bias is provided to electrodes 916 and 918 through circuit 926 by source 924 which may range from 0.1 to about 3 VDC depending upon the compound dissociation requirement and occasional needs for increased voltage to overcome insulating films that form. Hydrogen is ducted to collection and delivery to separator 904 by travel along the more or less conical surface 925, which may be a conductive surface depending upon the desired series/parallel variations or contained and supported by insulator 930 as shown.

[0096] In operation, liquors are mingled in distributor annulus 922 and travel upwards to provide process reactants and nutrients to microorganisms hosted in activated carbon cloth and/or granules 940 and 942 and or conductive felts that encase and substantially retain such granules proximate to electrode 916 and or 918. Smaller particles

and filaments may be added to infiltrate locations throughout the electrolyzer system to enhance electrical charge conductivity, enzyme, and catalytic functions including those previously disclosed. Separator 902 may be a reverse osmosis membrane or a cation or anion exchange membrane or it may be constructed according to the embodiments shown in Figures 2, 3, 4, or 5 and in some instances such separators may be used in conjunction with each other as may be desired to provide for various liquor circulation pathways and/or to produce hydrogen and carbon dioxide at different pressures or with a pressure differential between hydrogen and carbon dioxide.

[0097] Similarly, numerous circulation options are available if electrode 916 along with adjacent felt and or media 940 operate as electron sources to produce hydrogen from ions delivered from liquors that are circulated by the action of gas production lifts, convection currents, or by pump deliveries as shown. In this option, carbon dioxide is released as hydrogen ions are produced from acids delivered from 902 and 950 or that are produced by microorganisms hosted in fibrous or granular media 942 and associated felt materials that are electrically biased by electrode 918 to be opposite to electrode 916 as shown. Another exemplary option results if electrons are supplied by electrode 918 to produce hydrogen that is collected by insulator 930 for delivery to gas collector 904 as shown. In this instance electrode 916 and the media electrically associated with it are electron collectors as carbon dioxide is released to provide pumping in the fluid circuit shown as carbon dioxide is delivered past insulator 930 to collector 906 as shown.

[0098] Referring to Figure 7, system 900 can be used for converting organic feedstocks such as those produced by photosynthesis into methane, hydrogen, and/or carbon dioxide and/or by microorganisms. Depending upon the microorganisms that are hosted, liquors that typically include acids such as acetic and butyric acids along with compounds

such as urea are dissociated in electrolyzer 914. Electrolyzer 914 provides current at sufficient voltage to produce hydrogen from such compounds and acids and may provide operation as a digester and an electrolyzer, or may be operated within an anaerobic digester (not shown) or may utilize liquors produced by anaerobic digestion in 914 as shown. Such operation is particularly useful for converting organic wastes from a community and or industrial park for purposes of supplying the community with fuel and feed stocks for manufacturing carbon enhanced durable goods.

[0099] Although the invention has been described with respect to specific embodiments and examples, it will be readily appreciated by those skilled in the art that modifications and adaptations of the invention are possible without deviation from the spirit and scope of the invention. Accordingly, the scope of the present invention is limited only by the following claims.

CLAIMS

What is claimed is:

1. An electrolytic cell comprising:

a containment vessel;

a first electrode;

a second electrode;

a source of electrical current in electrical communication with the first electrode and the second electrode;

an electrolyte in fluid communication with the first electrode and the second electrode;

a gas, wherein the gas is formed during electrolysis at or near the first electrode;

a gas extraction area; and

a separator wherein separator comprises a substantially continuous helical configuration having two inclined surfaces forming a "V" shape;

wherein the separator directs flow of the electrolyte and the gas due to a difference between density of the electrolyte and the combined density of the electrolyte and the gas such that the gas substantially flows in a direction distal to the second electrode, and wherein the separator is further configured to promote circulation of the electrolyte between the first electrode, the gas extraction area, and the second electrode to provide fresh electrolyte to the first electrode and the second electrode.

2. The electrolytic cell of claim 1 wherein the separator comprises the first electrode.

3. The electrolytic cell of claim 2 wherein the separator further comprises a dielectric material.

4. The electrolytic cell of claim 3 further comprising a microorganism, wherein the separator substantially retains the microorganism in a desired location.

5. The electrolytic cell of claim 1 wherein the first electrode and the second electrode are configured to allow the polarity of the first electrode and the second electrode to reverse.

6. The electrolytic cell of claim 1 wherein the separator comprises the first electrode and the first electrode comprises a first conductive material proximal to the source of electrical current and a dielectric material distal to the source of electrical current.

7. The electrolytic cell of claim 6 wherein the first electrode further comprises a second conductive material proximal to the dielectric material and distal to the source of electrical current.

8. The electrolytic cell of claim 1 wherein the first electrode comprises a spring structure for vibration to promote release of nucleated gas from the electrodes

9. The electrolytic cell of claim 1 wherein the first electrode is configured to vibrate at a rate to promote circulation of the electrolyte.

10. An electrolytic cell comprising:

a containment vessel;

a first electrode;

a second electrode;

a source of electrical current in electrical communication with the first electrode and the second electrode;

an electrolyte in fluid communication with the first electrode and the second electrode;

a gas, wherein the gas is formed during electrolysis at or near the first electrode;

a gas extraction area; and

a separator wherein separator comprises two inclined surfaces forming a "V" shape, wherein the separator directs flow of the electrolyte and the gas due to a difference between density of the electrolyte and the combined density of the electrolyte and the gas such that the gas substantially flows in a direction distal to the second electrode, and wherein the separator is further configured to promote circulation of the electrolyte between the first electrode, the gas extraction area, and the second electrode to provide fresh electrolyte to the first electrode and the second electrode.

11. The electrolytic cell of claim 10 wherein the separator comprises the first electrode.

12. The electrolytic cell of claim 11 wherein the separator further comprises a dielectric material.

13. The electrolytic cell of claim 10 wherein separator comprises a substantially continuous helical configuration.

14. The electrolytic cell of claim 10 wherein separator comprises a substantially continuous multiple start helical configuration.

15. The electrolytic cell of claim 10 further comprising a microorganism, wherein the separator substantially retains the microorganism in a desired location.

16. The electrolytic cell of claim 10 wherein the first electrode and the second electrode are configured to allow the polarity of the first electrode and the second electrode to reverse.

17. The electrolytic cell of claim 10 wherein the separator comprises the first electrode and the first electrode comprises a first conductive material proximal to the source of electrical current and a dielectric material distal to the source of electrical current.

18. The electrolytic cell of claim 17 wherein the first electrode further comprises a second conductive material proximal to the dielectric material and distal to the source of electrical current.

19. The electrolytic cell of claim 10 wherein the first electrode comprises a spring structure for vibration to promote release of nucleated gas from the electrodes

20. The electrolytic cell of claim 19 wherein the first electrode is configured to vibrate at a rate to promote circulation of the electrolyte.

21. An electrolytic cell comprising:

a containment vessel;

a first electrode;

a second electrode;

a source of electrical current in electrical communication with the first electrode and

the second electrode;

an electrolyte in fluid communication with the first electrode and the second electrode;

a gas, wherein the gas is formed during electrolysis at or near the first electrode; and

a separator;

wherein the separator includes an inclined surface to direct flow of the electrolyte and the gas due to a difference between density of the electrolyte and the combined density of the electrolyte and the gas such that the gas substantially flows in a direction distal to the second electrode.

22. The electrolytic cell of claim 21 further comprising a gas extraction area wherein the separator is configured to promote circulation of the electrolyte between the first electrode, the gas extraction area, and the second electrode to provide fresh electrolyte to the first electrode and the second electrode.

23. The electrolytic cell of claim 22 wherein the separator comprises the first electrode.

24. The electrolytic cell of claim 23 wherein the separator further comprises a dielectric material.

25. The electrolytic cell of claim 22 wherein separator comprises two inclined surfaces forming a "V" shape.

26. The electrolytic cell of claim 25 wherein separator comprises at least two stacked plates, wherein each stacked plate comprises two inclined surfaces forming a "V" shape.

27. The electrolytic cell of claim 25 wherein separator comprises a substantially continuous helical configuration having an inclined surface.

28. The electrolytic cell of claim 25 wherein separator comprises a substantially continuous multiple start helical configuration having an inclined surface.

29. The electrolytic cell of claim 22 further comprising a microorganism, wherein the separator substantially retains the microorganism in a desired location.

30. The electrolytic cell of claim 22 wherein the first electrode and the second electrode are configured to allow the polarity of the first electrode and the second electrode to reverse.

31. The electrolytic cell of claim 22 wherein the separator comprises the first electrode and the first electrode comprises a first conductive material proximal to the source of electrical current and a dielectric material distal to the source of electrical current.

32. The electrolytic cell of claim 31 wherein the first electrode further comprises a second conductive material proximal to the dielectric material and distal to the source of electrical current.

33. The electrolytic cell of claim 22 wherein the first electrode comprises a spring structure for vibration to promote release of nucleated gas from the electrodes

34. The electrolytic cell of claim 33 wherein the first electrode is configured to vibrate at a rate to promote circulation of the electrolyte.