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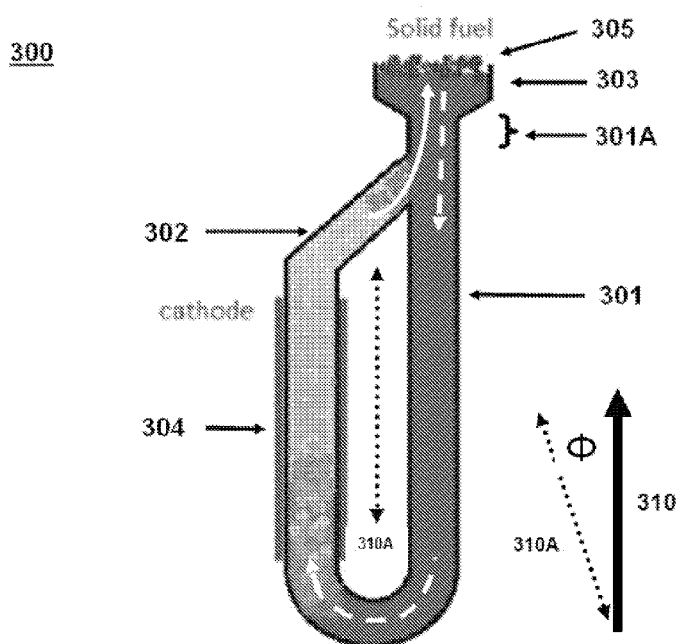
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(54) Title: DIRECT CARBON FUEL CELL AND STACK DESIGNS

FIG. 3A



(57) Abstract: Disclosed are novel configurations of Direct Carbon Fuel Cells (DCFCs), which optionally comprise a liquid anode. The liquid anode comprises a molten salt / metal, preferably Sb, and a fuel, which has significant elemental carbon content (coal, biomass, etc.). The supply of fuel is continuously replenished in the anode. In addition, a stack configuration is suggested where combining a large number of planar or tubular fuel elements.

DIRECT CARBON FUEL CELL AND STACK DESIGNS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Patent Application Ser. No. 61/815,302 filed April 24, 2013, which is incorporated by reference in its entirety.

GOVERNMENT RIGHTS

[0002] The subject matter disclosed herein was supported as part of the Catalysis Center for Energy Innovation, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award No. DE-SC0001004. The Government has certain rights in the herein disclosed subject matter.

TECHNICAL FIELD

[0003] This disclosure is in the field of energy generation and storage, including direct carbon fuel cells and stacks, and methods of operating the same.

BACKGROUND

[0004] Recently, researchers have been working to develop technology capable of efficiently producing energy from cheap and abundant solid carbonaceous fuel resources, like coal and renewable biomass. Much research has been devoted to developing direct carbon fuel cells (DCFCs) to electrochemically convert solid carbonaceous fuels to electricity.

[0005] The present inventions are directed to improvements in this technology field.

SUMMARY

[0006] Certain embodiments of the present invention provide direct carbon fuel cells, each of which comprises

(a) a chamber, comprising:

(i) a first columnar structure oriented along a first substantially vertical axis;

(ii) a second columnar structure comprising a wall, at least a portion of which comprises a solid non-porous oxide electrolyte capable of selectively transporting oxide ions through said wall, said second columnar structure oriented along a second substantially vertical axis;

(b) a vessel positioned above and in direct fluid communication with the first columnar structure, said vessel capable of containing a carbonaceous fuel; and

(c) a cathode adjacent to at least a portion of the solid non-porous oxide electrolyte of the second columnar structure,

said chamber being configured as a container such that the first and second columnar structures are in fluid communication with one another so as to allow fluid circulation therebetween.

[0007] Further embodiments include fuel cells further comprising an anode comprising a metal or metalloid that is molten and electrically conductive during the operation of the fuel cell. In some of these embodiments, these metals include molten metallic antimony or lead, preferably antimony. The invention further provides embodiments including various aspects of the vessel and the fuel(s) contained therein, and the anode. Specific descriptions are provided elsewhere herein for the structure, orientation, and materials associated with each of the columnar structures, the cathode, the current collectors, and contemplated operating temperatures.

[0008] Additional embodiments provide operating direct carbon fuel cells, each of which when operating comprises a circulating molten anode metal / metal oxide, said circulation driven by (a) cathode oxidation of a molten anode metal to a less dense molten metal oxide within the second columnar structure, (b) said less dense molten metal oxide then being carried by buoyant forces upward in the second columnar structure into the first columnar structure and into contact with a carbonaceous fuel contained within the vessel positioned above and in fluid communication with the first columnar structure, (c) whereupon the molten metal oxide oxidizes the carbonaceous fuel and itself is reduced to the denser molten anode metal, (d) at or after which time the denser anode metal sinks within the first columnar structure to provide a source for additional anode metal to be (e) drawn into the second columnar structure from a bottom portion of the second columnar structure to repeat the cycle.

[0009] Also provided are stack configuration embodiments, which configurations may comprise a plurality of direct carbon fuel cells, said fuel cells individually configured as provided elsewhere herein, wherein the vessels are capable of containing a carbonaceous fuel are in fluid communication with one another.

[0010] This disclosure also provides embodiments for operating the fuel cell or stacks, each method comprising a circulating molten anode / anode oxide, said method comprising (a) electrically reducing oxygen at the cathode to produce O^{2-} anions; (b) said fuel cell configured to conduct the O^{2-} anions through the solid non-porous oxide electrolyte to oxidize a molten anode

metal to form a buoyant molten anode metal oxide and to convectively transport the buoyant molten anode metal oxide to the vessel containing a carbonaceous fuel, where the carbonaceous fuel is oxidized and the molten anode metal oxide is reduced; and (c) collecting the electrons generated with the oxidation of the carbonaceous fuel at a first current collector and directing them to the cathode.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The present application is further understood when read in conjunction with the appended drawings. For the purpose of illustrating the subject matter, there are shown in the drawings exemplary embodiments of the subject matter; however, the presently disclosed subject matter is not limited to the specific methods, devices, and systems disclosed. In addition, the drawings are not necessarily drawn to scale. In the drawings:

[0012] **FIG. 1** illustrates a configuration of a direct carbon (or solid oxide) fuel cell system, where the cathode- electrolyte bilayer is attached at the bottom of an Al_2O_3 tube. The Sb anode rests above the electrolyte, under a bed of sugar char fuel. The cell was placed vertically in a tubular furnace. See Jayakumar, *et al.*, *Energy & Environmental Science*, 2011, 4, 4133, incorporated by reference herein in its entirety for all purposes.

[0013] **FIG. 2** provides an expanded view of **FIG. 1** for a fuel cell with molten Sb anode and solid carbonaceous fuel. Oxygen from air reacts with electrons at the conductive LSF-ScSZ (lanthanum-strontium-iron oxide /scandium stabilized zirconia) cathode and the O^{2-} ions are then transported through the ScSZ electrolyte. These ions oxidize the Sb anode at the electrolyte interface to form Sb_2O_3 , which moves through the bulk of the anode to contact the surface of the solid fuel. Reduction of the Sb_2O_3 by the fuel regenerates the Sb anode.

[0014] **FIG. 3** provides schematic representations of two illustrative embodiment of the present invention. **FIG. 3A** illustrates one embodiment of a single cell, where the darker color in the right tubular structure is meant to represent metallic Sb, while the lighter colors in the left tubular structure is intended to show a higher presence of oxide. **FIG. 3B** illustrates one possible stack configuration.

[0015] **FIG. 4** illustrates another cut-away schematic of an embodiment of the present invention, in which an alumina columnar structure and the liquid anode is contained within a YSZ columnar structure / alumina container, and the cathode is positioned adjacent to the YSZ tube.

[0016] FIG. 5 illustrates yet another cut-away schematic of an embodiment of the present invention, in which an alumina columnar structure is contained within a YSZ columnar structure, and the cathode is positioned adjacent to the YSZ structure.

[0017] FIG. 6 provides a schematic representation of the experimental apparatus used in the Examples. See **Example 1**.

[0018] FIG. 7 shows the long term performance plot for the DCFC with a pure Sb anode and an ScSZ electrolyte. The DCFC was run on 3 different solid fuels, pyrolyzed bio-oil, pyrolyzed rice starch, and activated charcoal. Current was generated at a constant voltage of 0.5 V. See **Example 2.1**.

[0019] FIG. 8 shows the long term performance plot for the DCFC with an Sb-Bi alloy anode and an ScSZ electrolyte. The DCFC was run on 3 different solid fuels, pyrolyzed bio-oil, pyrolyzed rice starch, and activated charcoal. Current was generated at a constant voltage of 0.5 V. See **Example 2.1**.

[0020] FIG. 9 shows V-I polarization curves for the DCFC with a pure Sb anode and an ScSZ electrolyte. See **Example 2.1**.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0021] The present invention may be understood more readily by reference to the following description taken in connection with the accompanying Figures and Examples, all of which form a part of this disclosure. It is to be understood that this invention is not limited to the specific products, methods, conditions or parameters described and / or shown herein, and that the terminology used herein is for the purpose of describing particular embodiments by way of example only and is not intended to be limiting of any claimed invention. Similarly, unless specifically otherwise stated, any description as to a possible mechanism or mode of action or reason for improvement is meant to be illustrative only, and the invention herein is not to be constrained by the correctness or incorrectness of any such suggested mechanism or mode of action or reason for improvement. Throughout this text, it is recognized that the descriptions refer to both fuel cells and methods of operating such fuel cells and associated systems. That is, where the disclosure describes and/or claims a feature or embodiment associated with a fuel cell, that feature or embodiment also refers to the method of operating such a fuel cell, and vice versa.

[0022] In the present disclosure the singular forms “a,” “an,” and “the” include the plural reference, and reference to a particular numerical value includes at least that particular value, unless the context clearly indicates otherwise. Thus, for example, a reference to “a

material” is a reference to at least one of such materials and equivalents thereof known to those skilled in the art, and so forth.

[0023] When a value is expressed as an approximation by use of the descriptor “about,” it will be understood that the particular value forms another embodiment. In general, use of the term “about” indicates approximations that can vary depending on the desired properties sought to be obtained by the disclosed subject matter and is to be interpreted in the specific context in which it is used, based on its function. The person skilled in the art will be able to interpret this as a matter of routine. In some cases, the number of significant figures used for a particular value may be one non-limiting method of determining the extent of the word “about.” In other cases, the gradations used in a series of values may be used to determine the intended range available to the term “about” for each value. Where present, all ranges are inclusive and combinable. That is, references to values stated in ranges include every value within that range.

[0024] When a list is presented, unless stated otherwise, it is to be understood that each individual element of that list and every combination of that list is to be interpreted as a separate embodiment. For example, a list of embodiments presented as “A, B, or C” is to be interpreted as including the embodiments, “A,” “B,” “C,” “A or B,” “A or C,” “B or C,” or “A, B, or C.”

[0025] It is to be appreciated that certain features of the invention which are, for clarity, described herein in the context of separate embodiments, may also be provided in combination in a single embodiment. That is, unless obviously incompatible or specifically excluded, each individual embodiment is deemed to be combinable with any other embodiment(s) and such a combination is considered to be another embodiment. Conversely, various features of the invention that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any sub-combination. Finally, while an embodiment may be described as part of a series of steps or part of a more general structure, each said step or part may also be considered an independent embodiment in itself.

[0026] The present invention relates to designs and configurations of reactors for use as fuel cell. Solid oxide fuel cells (SOFC) are based on ceramic electrolytes that are oxygen-ion conductors. Because the electrolytes conduct oxygen ions, it is at least theoretically possible to carry out the electrochemical conversion of any combustible fuel, including liquid hydrocarbons or even solid fuels like coal. The generation of electrical power by direct utilization of various fuels in an SOFC would also provide significant benefits if it could be practiced on a large scale. The efficiency of an SOFC can be very high, with negligible NO_x emissions. Moreover, if CO₂ sequestration is required, the exhaust gas from the anode is highly concentrated, allowing for

easy CO₂ capture. Finally, direct utilization of hydrocarbon fuels greatly simplifies the overall conversion process by eliminating the need for gasification and steam reforming steps.

[0027] In any SOFC, O₂ from the air is reduced at the cathode to produce O²⁻ anions, according to Equation 1.



The O²⁻ ions then pass through the dense ceramic electrolyte, which must be an electronic insulator in order to generate current through movement of the O²⁻ anions only. Finally, the O²⁻ anions oxidize the fuel at the anode; if that fuel is carbon, the anode reaction is given by Equation 2).



The overall fuel-cell reaction is $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ but the electrons produced at the anode have a higher potential energy from those consumed at the cathode.

[0028] One such configuration for such a reactor is shown in **FIGs. 1 and 2**, and illustrate the use with molten Sb anodes. In this illustrative example, the direct utilization of carbonaceous fuels, including biomass, using a solid oxide (or direct carbon) fuel cell (SOFC) with a molten antimony (Sb) anode at intermediate temperatures (e.g., 973 K) operates by the oxidation of the metallic Sb at the electrolyte interface with the resulting Sb₂O₃ being reduced by the fuel in a separate step. The reduction of Sb₂O₃ is shown to occur readily by contact with a range of different carbonaceous fuels at the fuel cell operating temperature.

[0029] The performance of SOFC operating on carbon is almost always limited by the transfer of oxide ions from the electrolyte to the solid fuel. Various approaches have been taken to facilitate this transfer. The present invention relates to reactors which use molten-metal electrodes. The Examples provide some information on the use of molten Sb in these presented inventive reactor configurations. While molten Sb is attractive for the reasons described herein, it should be appreciated that the invention is not limited to this metal, and the range of materials useful in the present configurations are describe elsewhere herein. See also Jayakumar, *et al.*, *J. Electrochemical Soc.*, 157 (3), B365-369 (2010); Jayakumar, *et al.*, *J. Electrochemical Soc.*, 158 (12) B1472-1478 (2011); and Jayakumar, *et al.*, *J. Electrochemical Soc.*, 159 (4), A386-A389 (2012), each of which is incorporated by reference herein in its entirety for all purposes.

[0030] The present invention includes embodiments related to direct carbon fuel cells having very different and novel configurations relative to those previously described. In the following descriptions, reference is made to **FIGs. 3-5** (the following reference numbers are described in **FIG. 3**).

[0031] In certain of these embodiments, each direct carbon fuel cell comprises:

(a) a chamber **300** comprising:

(i) a first columnar structure **301** oriented along a first substantially vertical axis;

(ii) a second columnar structure **302** comprising a wall, at least a portion of which comprises a solid non-porous oxide electrolyte capable of selectively transporting oxide ions through said wall, said second columnar structure oriented along a second substantially vertical axis;

(b) a vessel **303** positioned above and in direct fluid communication with the first columnar structure, said vessel capable of containing a carbonaceous fuel;

(c) a cathode **304** adjacent to at least a portion of the solid non-porous oxide electrolyte of the second columnar structure;

said chamber configured as a container such that the first and second columnar structures are in fluid communication with one another so as to allow fluid circulation therebetween.

[0032] In this latter aspect, a bottom portion of the second columnar structure is fluidically coupled to a bottom portion of the first columnar structure and an upper portion of the second columnar structure is fluidically coupled to an upper portion of the first columnar structure so as to form a fluidic circuit. See, *e.g.*, **FIGs. 3A, 4, and 5**. The fluidic coupling at the upper portion of the first columnar structure **301** may be positioned either at a position below the vessel capable of containing a carbonaceous fuel (*e.g.*, displaced by a distance **301A** in **FIG. 3A**) or directly to the vessel.

[0033] Throughout this specification, words are to be afforded their normal meaning, as would be understood by those skilled the relevant art. However, so as to avoid misunderstanding, the meanings of certain terms will be specifically defined or clarified.

[0034] For example, in the descriptions herein, the term “columnar structure” is not intended to connote any particular aspect ratio; *i.e.*, the ratio of length to width of the columnar structure can be less about 1, about 1, or greater than about 1. Rather, it is intended to connote the importance of substantially vertical orientation, so as to allow and/or promote a natural convective flow during operation of the fuel cell. As with respect to the cross-section of the first and second columnar structures, in certain embodiments, either or both have a cross-section that is round, oblong, oval, or polygonal (typically 4-, 5-, 6-, 8-, or 10- sided or higher) or a combination thereof. In certain of these embodiments, the presence of a flat surface along the second columnar structure allows for the use of planar cathodes, as desired.

[0035] Also as used herein, the term “substantially vertical” intended to connote that one end of the structure is physically lower than the other end; said structures may be substantially linear (as illustrated in **FIG. 3A**, element **301**), bent (as illustrated in **FIG. 3A**, element **302**) or curved or have one or more elements, each of which are linear or curved. Unless otherwise described, a structure is considered to be “substantially vertical” if a line constructed between the upper and lower ends is within 45° of a line of buoyancy as shown in **310**. “Line of buoyancy” is the direction an air bubble would travel in water (or any less dense material in a more dense fluid, e.g., Sb_2O_3 in Sb), if otherwise unperturbed by external forces (e.g., stirring, electromotive fields, etc.) and reflects a true vertical line defined by gravity (e.g., **310**). Referring to **FIG. 3A**, the dotted line **310A** within reflects such a constructed line for fuel cell **300**, element **310** reflects a line of buoyancy, and the angle, Φ , describes the angle therebetween. Other embodiments provide that this angle, Φ , is in a range of from about 0° (i.e., parallel with the line of buoyancy) to about 70° , to about 60° , to about 50° , to about 40° , to about 30° , to about 20° , or to about 10° of a line of buoyancy. In certain embodiments, at least one of the first and second substantially vertical axes are aligned parallel with a line of buoyancy **310** (e.g., $\Phi = 0$). In some embodiments, both axes are aligned parallel with a line of buoyancy **310**. In other embodiments, at least one of the first and second substantially vertical axes are at different orientations with respect to the line of buoyancy.

[0036] The fuel cell, chamber, and container may each hold a solid, liquid, gas, or combination thereof, and be constructed of materials suitable for its intended use as a direct carbon fuel cell. The fuel cell should be capable of withstanding temperatures in a range of from about 600K to about 1150K, preferably 950K to about 1150K. Without being bound to any particular theory, such a criterion tends to favor ceramic oxides at least for the materials used in the columnar structures.

[0037] As described, the inventive cells each include at least one second columnar structure comprising a wall, at least a portion of which comprises a solid non-porous oxide electrolyte capable of selectively transporting oxide ions through said wall. While such electrolytes are known by those skilled in the art, in various embodiments, such solid oxide electrolytes comprises one or more oxides of Hf, Zr, Y, Sc, Yb, La, Ga, Gd, Bi, Ce, and Th, optionally doped with oxides from the group consisting of alkaline earth metals and rare earth metals. In some embodiments, the solid oxide electrolyte comprises zirconia, for example doped with Y or Sc. (e.g., YSZ or ScSZ). Depending on the nature of the molten anode metal and/or metal oxide, it may be desirable in some embodiments to coat at least one surface (e.g., the

surface contacting the molten anode) with an oxide barrier layer (e.g., Ca- or Mg-doped zirconia or doped ceria) to improve chemical corrosion resistance or embrittlement.

[0038] The fuel cells of the present invention also comprise a cathode **304** which itself typically comprises a ceramic metal oxide. Again, such materials are commonly used as SOFC cathodes and known by those skilled in the art. In certain embodiments, these comprise a lanthanum-strontium-manganese oxide (LSM) or a lanthanum-strontium-iron oxide (LSF), e.g., $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ or $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, or other oxides.

[0039] The positioning of the cathode is typically directly adjacent to the solid non-porous electrolyte of the second columnar structure, for example as configured and positioned as shown within the figures.

[0040] In certain embodiments, the fuel cell further comprises an anode comprising a metal (or metalloid) which is molten and electrically conductive while within the temperature ranges described herein, including during the operation of the fuel cell. While the anode may comprise a metal or metalloid, for the sake of brevity, the term “metal” or “metallic” is used to reflect a material that meets these conditions. The chamber / container suitably sustainably contains the liquid / molten anode during the operation of the cell (the terms “liquid” and “molten” are practically interchangeable in the present context). In certain of these embodiments, the metal (or metalloid) forms a thermodynamically stable oxide which is also liquid / molten and less dense than the molten anode metal at a temperature in a range of from about 500K to about 1200K. Other embodiments provide that the anode metal and metal oxide are both liquid over a temperature range bounded at the lower end by a value of about 500, 550, 600, 650, 700, 750, or 800K and at the upper end by a value of about 1200, 1150, 1100, 1050, 1000, 950, or 900K. The anode may comprise metallic antimony or lead (including their respective oxides), and is preferably antimony. While antimony / antimony oxide (Sb_2O_3) is a preferred anode material pair, the anodes may also include alloys, both of Sb and Pb and potentially with Ag and Bi, and/or with metals that reduce more easily than Sb.

[0041] Antimony, Sb, is attractive, in part, because both Sb (melting point 903 K) and Sb_2O_3 (melting point 929 K) have melting points below the temperatures typically used for operation of the fuel cells, 973 to 1073 K, which precludes the formation of a solid oxide film at the electrolyte-anode interface (as happens in corresponding Sn systems). The impedance of molten Sb electrodes is also very low, less than $0.1 \Omega\text{cm}^2$ at 973 K, and is reasonably independent of the Sb / Sb_2O_3 ratio. The Nernst Potential for Sb oxidation is lower compared to that for carbon oxidation, 0.75 V versus ~1 V at 973 K. Although this lower OCV does represent a loss of available energy for producing electricity, the lost electrical energy would still be

available as high-quality heat. The high thermal conductivity of the molten metal makes it possible to operate the cell isothermally and to collect the high-quality heat efficiently.

Furthermore, the anode impedance associated with Sb oxidation is so low that it is still possible to operate cells at reasonable potentials. Finally, the difference in oxidation potentials between carbon and Sb makes the reduction of Sb_2O_3 by the solid carbonaceous fuels thermodynamically spontaneous.

[0042] Embodiments of the fuel cells are described as including a vessel **303** positioned above and in direct fluid communication with the first columnar structure, said vessel capable of containing a carbonaceous fuel. In certain embodiments, the vessel contains a carbonaceous fuel and is configured to place the carbonaceous fuel into physical contact with the anode during operation of the fuel cell. As contemplated herein, the carbonaceous fuel may be derived from biomass or waste fuels. Non-limiting examples of such carbonaceous fuels include materials derived from pulverized coal, charcoal, peat, coke, char, petroleum coke, oil sand, tar sand, waste plastics, biomass, and carbon produced by pyrolysis of a carbonaceous substance. In some embodiments, the carbonaceous fuel comprises sugar char, rice starch, carbon black, or a combination thereof, each of which is preferably at least partially dehydrated before being placed in contact with the molten anode. It is also preferred, but not necessarily required, that the carbonaceous fuel can be oxidized at temperatures below about 1000K.

[0043] In certain embodiments, the fuel cell further comprises a device (e.g., at least one fan blade, paddle, or skimmer) for mixing the interface between the fuel and molten anode oxide, so as to at least partially break up or remove any “ash” layer that can form at the carbon-Sb interface with some of the fuels during the operation of the cell.

[0044] In some embodiments, the fuel cell further comprising (a) a first current collector positioned within the first columnar structure, capable of being in electrical communication with a molten anode during the operation of the fuel cell; (b) a second current collector in electrical communication with the cathode; or (c) both (a) and (b). Where present, the first and second current conductors should be corrosion resistant within their respective environments. Exemplary current conductors are those materials comprising Au, Ag, Re, Mo, Pd, Pt, W, graphite, or a combination thereof. The first current conductor, in contact with the molten anode, is suitably capable of withstanding chemical degradation on contact with anode or anode oxide. In the case of Sb / Sb_2O_3 , Re is one such material. The choice of the material for the second current collector, when remote from the anode material includes a variety of materials, including silver.

[0045] To this point, the embodiments have been described in terms of individual first and second columnar structures, where the first columnar structure may be located external to the second columnar structure (e.g., FIG. 3A), but as shown in FIG. 3B, 4, and 5, the invention is not so limited. As exemplified in FIG. 3B, in certain embodiments each cell may comprise multiple first or second columnar structures, each located external to the others. For example, the cells may be arranged so that each chamber comprises a plurality of second columnar structures, each having a wall at least a portion of which comprises a solid non-porous oxide electrolyte (and cathode), each second columnar structure oriented along a corresponding substantially vertical axis, and each in fluid communication with the first columnar structure. Further, as shown in FIG. 3B, stacks of cells may be constructed from multiple individual cells, for example, by configuring the cathode from the first cell in contact with the anode from the next, so as to achieve a stack with a higher output voltage. Stacks may also be configured by having the carbonaceous carbon vessels of each cell in physical contact / fluid communication with one another, for example in serial arrangement. That is, additional embodiments provide for stack configurations of these inventive cells, each stack configuration comprising a plurality of direct carbon fuel cells, said fuel cells individually configured as described herein, wherein the vessels capable of containing a carbonaceous fuel are in fluid communication with one another.

[0046] In other embodiments, a first columnar structure is located within and/or contained by the second columnar structure. Such embodiments are exemplified in the schematic structures shown in FIGs. 4 and 5. In other embodiments, multiple first columnar structures, each comprising a solid oxide electrolyte and each oriented along a corresponding substantially vertical axis are in fluid communication and positioned within a second columnar structure.

[0047] EXAMPLES

[0048] **Overview:** The following experiments illustrate the long term stability of solid oxide fuel cells (SOFC) that utilize solid carbonaceous fuels with molten Sb and Sb-Bi alloy anodes at 973 K. The operation of these direct carbon fuel cells (DCFC) involved the oxidation of metallic Sb at the electrolyte-anode interface to produce molten Sb_2O_3 , which was then reduced by the fuel in a separate step. The cell performance duration, however, with traditional solid fuels is severely limited by the formation of an ash layer on the surface of the partially oxidized solid fuel particles, which prevents further fuel utilization. This issue is resolved by stirring the anode-fuel interface to shear away the ash layer. Such DCFCs can generate energy at high power densities for >200 hours with periodic stirring. The three different solid fuels used were a pyrolyzed bio-oil, pyrolyzed rice starch, and activated charcoal. During these tests, the

ohmic resistance decreased with time below that expected for the Sc_2O_3 -stabilized ZrO_2 electrolyte's thickness. Inspection by scanning electron microscopy revealed the grain growth and subsequent depletion of the electrolyte at its interface with the anode. Y_2O_3 -stabilized ZrO_2 on the other hand, showed no thinning but underwent restructuring shown by grain formation.

[0049] Example 1: Experimental

[0050] Because the anodes in the fuel cells used here consisted simply of having the molten metal in contact with the bare electrolyte surface, the ceramic component of the cells consisted of just the electrolyte with cathode on one side. The cathode-electrolyte wafers were constructed using tape-casting methods that have been described in other papers. Briefly, tapes, with and without pore formers, were laminated and fired to produce a bilayer wafer of the electrolyte material with one side porous and the other dense. The circular porous layer was 0.67 cm in diameter while the dense electrolyte layer was 1.4 cm in diameter. The electronically conductive cathode was prepared from the porous layer by infiltration of nitrate salts to produce a composite that was 35-wt% LSF ($\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$). X-ray diffraction was used to confirm that the LSF had the proper perovskite structure following calcination to 1123 K.

[0051] The two electrolyte materials tested in this study were 10% Sc_2O_3 -stabilized ZrO_2 (ScSZ) and 8% Y_2O_3 -stabilized ZrO_2 (YSZ). Although ScSZ was significantly more expensive than YSZ, it was mechanically stronger and had a higher ionic conductivity. The cells made with ScSZ had 100- μm thick electrolytes, while the YSZ cells had electrolytes that were 160 μm thick, made by laminating two 80- μm tapes. In both ScSZ and YSZ cells, the porous cathode was 50 μm thick. The experimental apparatus is shown schematically in **FIG. 6** and was similar to that used in an earlier study of electrochemical energy storage, where mixing of the molten $\text{Sb}/\text{Sb}_2\text{O}_3$ mixture was critical. The fuel cell was attached to the end of an alumina tube with a ceramic adhesive (Aremco Ceramabond 552). Silver paste and wires were used to make electrical connections to the cathode. Next, metal powder was added into the alumina tube, making contact with the electrolyte surface by gravity. Experiments with pure Sb used 10 g of Sb powder (-100 mesh, 99.5%, Alfa Aesar), while experiments with the Sb-Bi alloy employed a mixture 8 g of Sb and 3.45 g of Bi (-100 mesh, 99%, Sigma-Aldrich) to produce an alloy that was 20-mol% Bi. Rhenium wires were inserted into the anode for current collection. After inserting an alumina stirring rod to the anode-fuel interface, the top end of the alumina tube was plugged with glass wool. Finally, the fuel cell was placed in a tube furnace and heated to 973 K. The powdered fuels added directly onto the anode. To assist in the addition of the biomass fuels, these were always added as a 40:60 mixture with charcoal (Supelco). Following an initial charge of 1.5 g of fuel, 0.5-g fuel additions were made every 6 to 10 hours of cell operation. Stirring of

the anode-fuel interface was carried out for 2 to 5 min before and after every fuel addition. To obtain a better measure of the amount of fuel that was added to the anode compartment, each of the fuels was briefly heated to 873 K in an inert gas in order to drive off volatile gases, prior to measuring the fuel weight added to the cell. In a typical 200-h experiment, the total amount of fuel added to the anode was approximately 13 g, of which approximately 5 g was recovered at the end of the experiment. As a point of reference, 4.0 g of pure C would be required to produce a current of 500 mA/cm^2 for 200 h, with the current density referenced to the active area of our cathodes, 0.353 cm^2 . The difference between the amounts of fuel that were consumed and the electron balance are partially associated with oxygen in the fuel and partially to remaining volatility in the fuel. The biomass fuels were rice starch (Sigma-Aldrich) and Bio-Oil. The Bio-Oil was provided by Renewable Oil International LLC (ROI) and was produced by fast pyrolysis of hardwood trees. The electrochemical and impedance measurements in this study were performed using a Gamry Instruments Potentiostat. Unless otherwise stated, the current densities reported in this paper were normalized to the external area of the cathodes. The impedance spectra were performed galvanostatically in the frequency range from 300 kHz to 0.1 Hz with an A.C. perturbation of 1 mA. Scanning electron microscopy (SEM) was performed using a JEOL 7500F HRSEM.

[0052] Example 2: Results

[0053] Example 2.1: Cells with ScSZ Electrolytes

[0054] FIGs. 7 and 8 show results from a 200-h experiment in which the current density, based on the external area of the cathode, was monitored while holding the cell potential at 0.5 V, with intermittent addition of various fuels. The arrows indicate the times at which 0.5 g increments of fuel (60-wt% charcoal, 40-wt% either rice starch or bio-oil) were added. The calculated power densities are reported on the right side. The cell in this study had a 100- μm ScSZ electrolyte, with an LSF-ScSZ composite cathode and 10 g of Sb as the anode. The current density initially drifted downward during the first 70 h, from a current density of 580 mA/cm^2 and power density of 290 mA/cm^2 , to a current density of 460 mA/cm^2 , after which the performance started to improve.

[0055] V-i polarization curves and impedance plots for the cell at 0 h, 100 h, and 200 h are shown in FIG. 9. The open-circuit voltage (OCV) was 0.75 V at all times, in agreement with the expected Nernst potential for Sb oxidation to Sb_2O_3 . However, the slope of the V-i relationship, also known as the specific cell resistance, did increase from an average initial value of $0.38 \Omega\text{cm}^2$ to $0.50 \Omega\text{cm}^2$ after 100 h. The V-I relationships at 100 and 200 h were virtually unchanged.

[0056] It should be appreciated that independent embodiments of the fuel cells of the present inventions include those configurations with or without the molten anode material, and either operating or not. One of the advantages of the present configurations is their ability to take advantage of buoyancy to drive the operation of the cell. Accordingly, various embodiments of the invention include operating direct carbon fuel cells, each configured as described in any of the relevant embodiments described herein, which when operating comprises a circulating molten anode metal / metal oxide, said circulation driven by (a) cathode oxidation of a molten anode metal to a less dense molten metal oxide within the second columnar structure, (b) said less dense molten metal oxide then being carried by buoyant forces upward in the second columnar structure into the first columnar structure and into contact with a carbonaceous fuel contained within the vessel positioned above and in fluid communication with the first columnar structure (*see, e.g.*, the curved line in **FIG 3A**), (c) whereupon the molten metal oxide oxidizes the carbonaceous fuel and itself is reduced to the denser molten anode metal, (d) at or after which time the denser anode metal sinks within the first columnar structure to provide a source for additional anode metal (*see, e.g.*, the dashed line in **FIG 3A**) to be (e) drawn into the second columnar structure from a bottom portion of the second columnar structure to repeat the cycle. These fuel cells, when operating, generates electrical current by the oxidation of the carbonaceous fuel by the molten anode metal oxide.

[0057] The present invention contemplates and includes methods of operating the disclosed direct carbon fuel cells. In certain of these embodiments, these methods comprise operating direct carbon fuel cell or cell stack configured as in any one of disclosed embodiments, which when operating comprises a circulating molten anode / anode oxide, said method comprising (a) electrically reducing oxygen (comprising air or oxygen enriched air) at the cathode to produce O^{2-} anions; (b) said fuel cell configured to conduct the O^{2-} anions through the solid non-porous oxide electrolyte to oxidize a molten anode metal to form a buoyant molten anode metal oxide and to convectively transport the buoyant molten anode metal oxide to the vessel containing a carbonaceous fuel, where the carbonaceous fuel is oxidized and the molten anode metal oxide is reduced; and (c) collecting the electrons generated with the oxidation of the carbonaceous fuel at a first current collector and directing them to the cathode.

[0058] As those skilled in the art will appreciate, numerous modifications and variations of the present invention are possible in light of these teachings, and all such are contemplated hereby. For example, in addition to the embodiments described herein, the present invention contemplates and claims those inventions resulting from the combination of features of the invention cited herein and those of the cited prior art references which complement the

features of the present invention. Similarly, it will be appreciated that any described material, feature, or article may be used in combination with any other material, feature, or article, and such combinations are considered within the scope of this invention. The disclosures of each patent, patent application, and publication cited or described in this document are hereby incorporated herein by reference, each in its entirety, for all purposes.

What is Claimed:

- 1) A direct carbon fuel cell, comprising:
 - (a) a chamber comprising:
 - (i) a first columnar structure oriented along a first substantially vertical axis;
 - (ii) a second columnar structure comprising a wall, at least a portion of which comprises a solid non-porous oxide electrolyte capable of selectively transporting oxide ions through said wall, said second columnar structure oriented along a second substantially vertical axis;
 - (b) a vessel positioned above and in direct fluid communication with the first columnar structure, said vessel capable of containing a carbonaceous fuel; and
 - (c) a cathode adjacent to at least a portion of the solid non-porous oxide electrolyte of the second columnar structure,

said chamber configured as a container such that the first and second columnar structures are in fluid communication with one another so as to allow fluid circulation therebetween.
- 2) The fuel cell of claim 1, further comprising an anode comprising a metal or metalloid which is molten and electrically conductive during the operation of the fuel cell.
- 3) The fuel cell of claim 2, wherein the metal or metalloid forms a thermodynamically stable oxide which is molten and less dense than the molten anode metal at a temperature in a range of from about 500 K to about 1200 K.
- 4) The fuel cell of claim 2, wherein the anode comprises metallic antimony or lead.
- 5) The fuel cell of any one of claims 1 to 4, wherein the vessel contains a carbonaceous fuel and is configured to place the carbonaceous fuel into contact with the anode during operation of the fuel cell.
- 6) The fuel cell of any one of claims 1 to 5, further comprising (a) a first current collector positioned within the first columnar structure, capable of being in electrical communication with a molten anode during the operation of the fuel cell; (b) a second current collector in electrical communication with the cathode; or (c) both (a) and (b).

- 7) The fuel cell of claim 1, wherein a bottom portion of the second columnar structure is fluidically coupled to a bottom portion of the first columnar structure and an upper portion of the second columnar structure is fluidically coupled to an upper portion of the first columnar structure so as to form a fluidic circuit
- 8) The fuel cell of any one of claims 1 to 7, wherein at least one of the first and second substantially vertical axes are aligned parallel with a line of buoyancy.
- 9) The fuel cell of any one of claims 1 to 8, wherein at least one of the first and second substantially vertical axes are at different orientations with respect to the line of buoyancy.
- 10) The fuel cell of any one of claims 1 to 9, wherein at least one of the first and second columnar structures have a round, oblong, oval, or polygonal cross-section.
- [11) The fuel cell of claim 1, wherein the first columnar structure is located external to the second columnar structure.
- 12) The fuel cell of claim 11, wherein the chamber comprises a plurality of second columnar structures, each having a wall at least a portion of which comprises a solid non-porous oxide electrolyte, each second columnar structure oriented along a corresponding substantially vertical axis, and each in fluid communication with the first columnar structure.
- 13) The fuel cell of claim 1, wherein the first columnar structure is located within the second columnar structure.
- 14) The fuel cell of claim 13, wherein the chamber comprises a plurality of first columnar structures, each comprising a solid oxide electrolyte, each oriented along a corresponding substantially vertical axis, and each in fluid communication with the second columnar structure.
- 15) The fuel cell of any one of claims 1 to 14, which when operating generates electrical current by the oxidation of the carbonaceous fuel by the molten anode metal oxide.
- 16) The fuel cell of any one of claims 1 to 15, wherein the solid oxide electrolyte comprises one or more oxides of Hf, Zr, Y, Sc, Yb, La, Ga, Gd, Bi, Ce, and Th, optionally doped with oxides from the group consisting of alkaline earth metals and rare earth metals.
- 17) The fuel cell of any one of claims 1 to 16, wherein the solid oxide electrolyte comprises zirconia.

- 18) The fuel cell of any one of claims 1 to 17, wherein at least one surface of the second columnar structure is coated with an oxide barrier layer.
- 19) The fuel cell of any one of claims 1 to 18, said cell capable of withstanding temperatures in a range of from about 600K to about 1150K.
- 20) The fuel cell of any one of claims 1 to 19, wherein the cathode comprises a ceramic metal oxide.
- 21) The fuel cell of claim 20, wherein the cathode comprises a lanthanum-strontium-manganese oxide or a lanthanum-strontium-iron oxide.
- 22) The fuel cell of any one of claims 1 to 21, wherein the anode and anode oxide are both liquid at a temperature in a range of from about 950K to about 1150K.
- 23) The fuel cell of any one of claims 1 to 22, wherein the first and second current conductors are corrosion resistant within their respective environments.
- 24) The fuel cell of any one of claims 1 to 23, wherein the first or second or both first and second current conductors comprise Au, Ag, Re, Mo, Pd, Pt, W, graphite, or a combination thereof.
- 25) The fuel cell of any one of claims 1 to 24, wherein the carbonaceous fuel can be oxidized at temperatures below about 1000K.
- 26) The fuel cell of any one of claims 1 to 25, wherein the carbonaceous fuel is derived from biomass or waste fuels.
- 27) The fuel cell of any one of the preceding claims, wherein the carbonaceous fuel comprises sugar char, rice starch, carbon black, or a combination thereof.
- 28) An operating direct carbon fuel cell configured as a fuel cell of claim 1, which when operating comprises a circulating molten anode metal / metal oxide, said circulation driven by (a) cathode oxidation of a molten anode metal to a less dense molten metal oxide within the second columnar structure, (b) said less dense molten metal oxide then being carried by buoyant forces upward in the second columnar structure into the first columnar structure and into contact with a carbonaceous fuel contained within the vessel positioned above and in fluid communication with the first columnar structure, (c) whereupon the molten metal oxide oxidizes the carbonaceous

fuel and itself is reduced to the denser molten anode metal, (d) at or after which time the denser anode metal sinks within the first columnar structure to provide a source for additional anode metal to be (e) drawn into the second columnar structure from a bottom portion of the second columnar structure to repeat the cycle.

29) A stack configuration comprising a plurality of direct carbon fuel cells, said fuel cells individually configured as in any one of claims 1 to 28, wherein the vessels capable of containing a carbonaceous fuel are in fluid communication with one another.

30) A method of operating direct carbon fuel cell or cell stack configured as in any one of claims 1 to 29, which when operating comprises a circulating molten anode / anode oxide, said method comprising (a) electrically reducing oxygen at the cathode to produce O^{2-} anions; (b) said fuel cell configured to conduct the O^{2-} anions through the solid non-porous oxide electrolyte to oxidize a molten anode metal to form a buoyant molten anode metal oxide and to convectively transport the buoyant molten anode metal oxide to the vessel containing a carbonaceous fuel, where the carbonaceous fuel is oxidized and the molten anode metal oxide is reduced; and (c) collecting the electrons generated with the oxidation of the carbonaceous fuel at a first current collector and directing them to the cathode.

FIG. 1

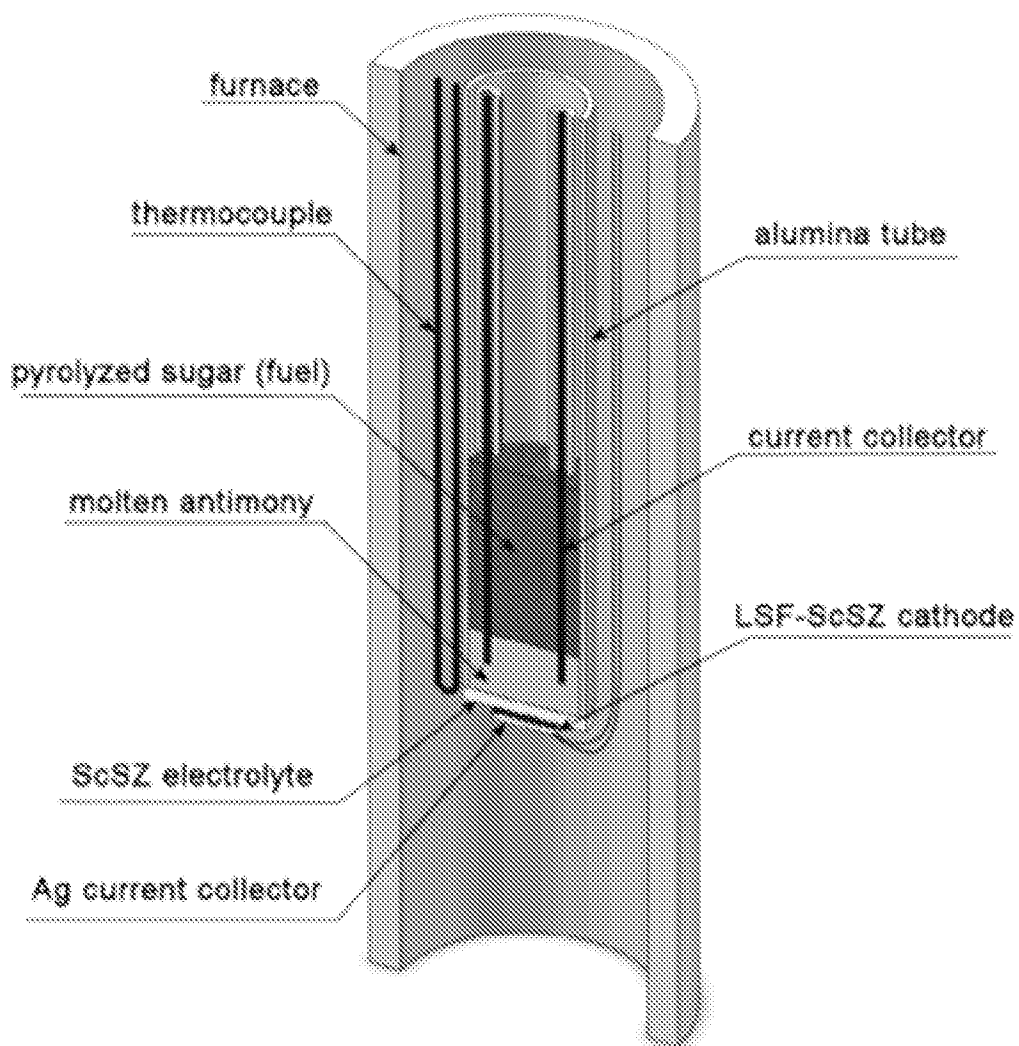
**PRIOR ART**

FIG. 2

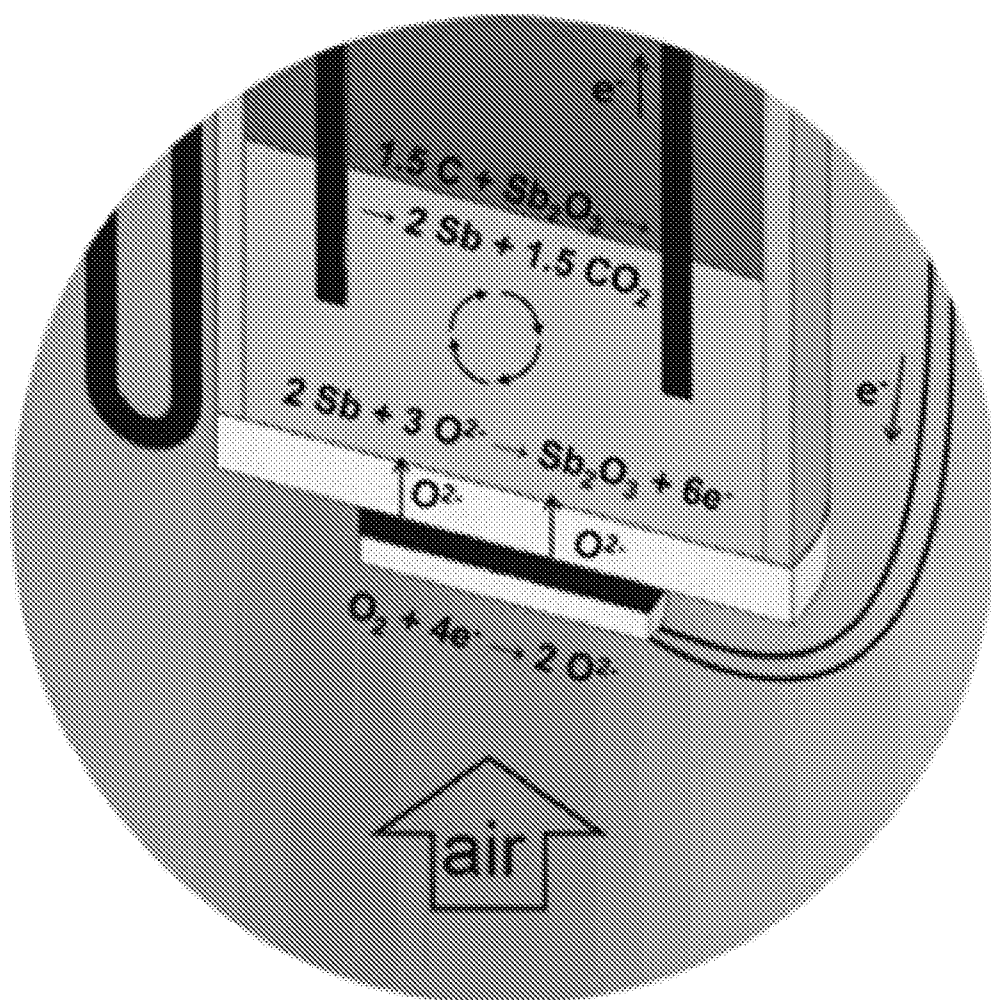
**PRIOR ART**

FIG. 3A

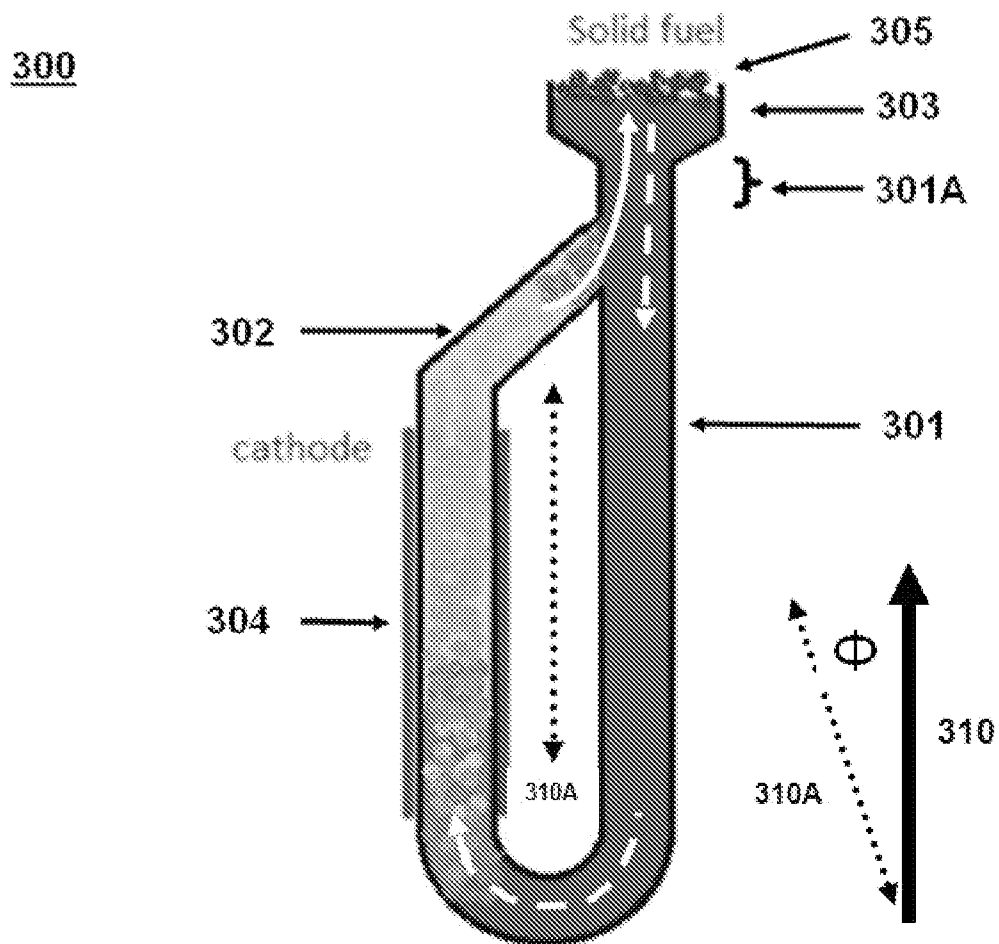


FIG. 3B

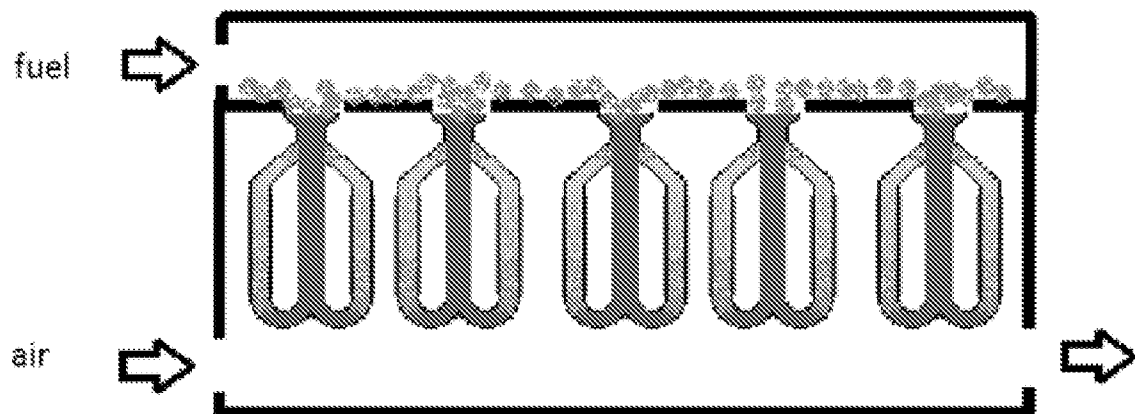


FIG. 4

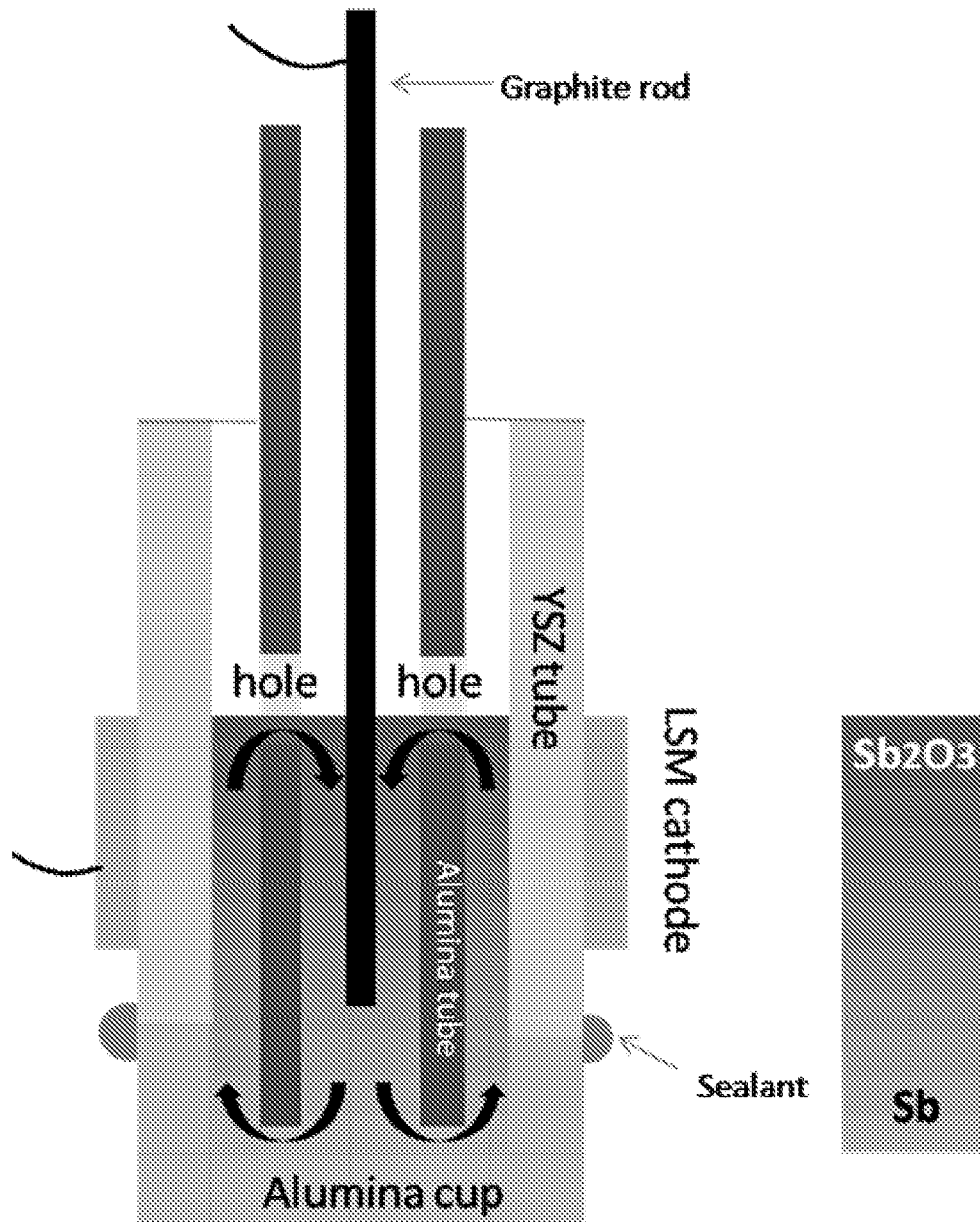


FIG. 5

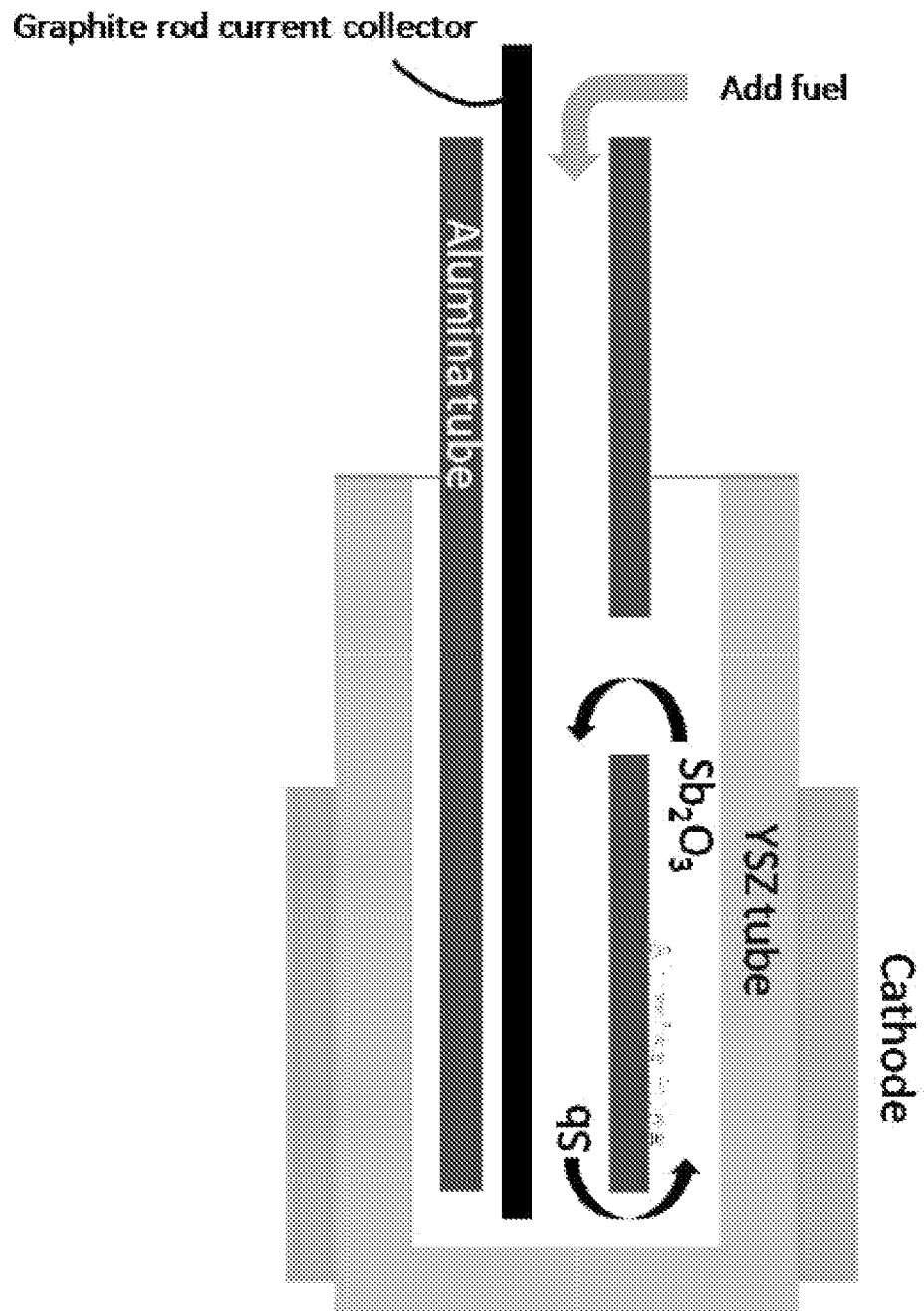


FIG. 6

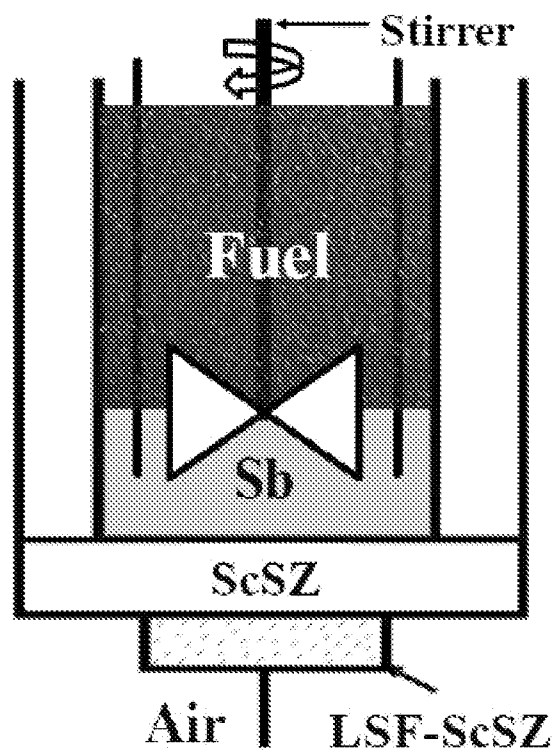


FIG. 7

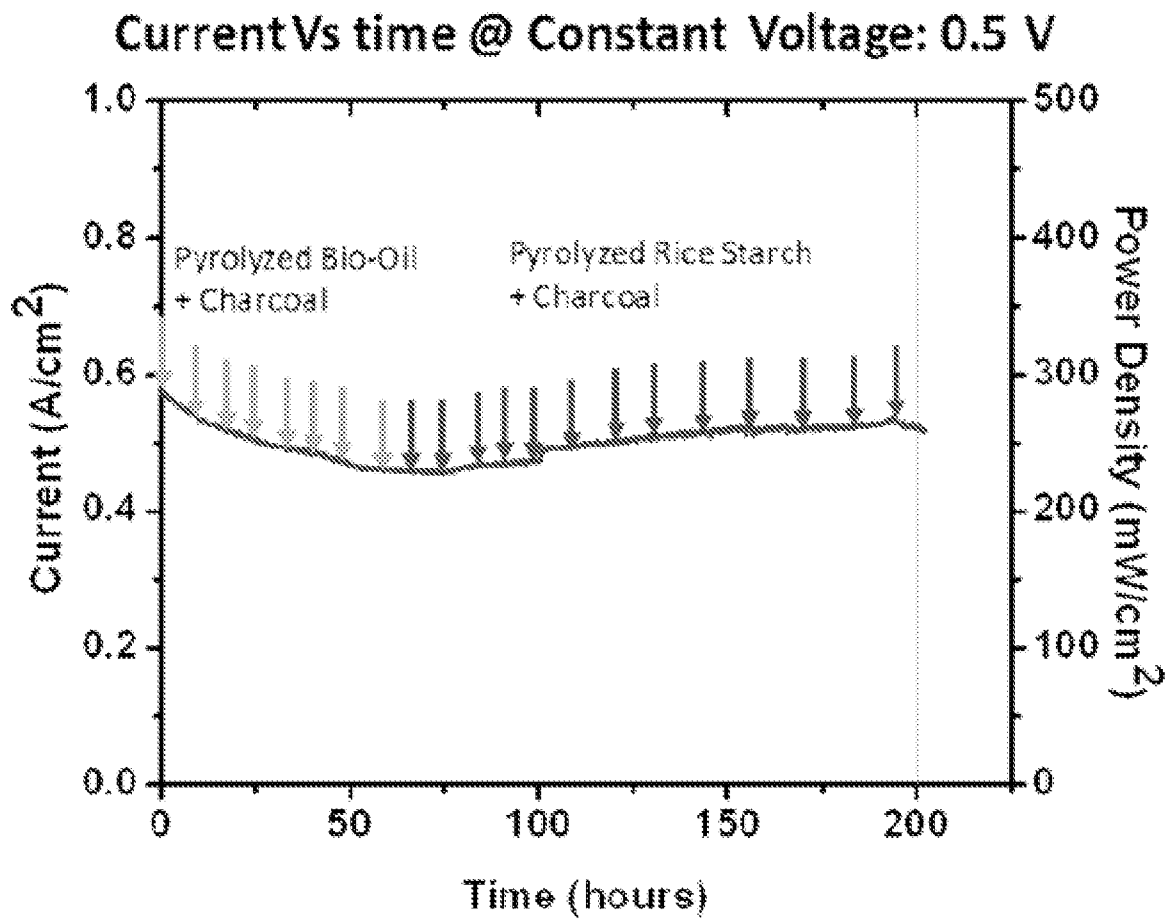


FIG. 8

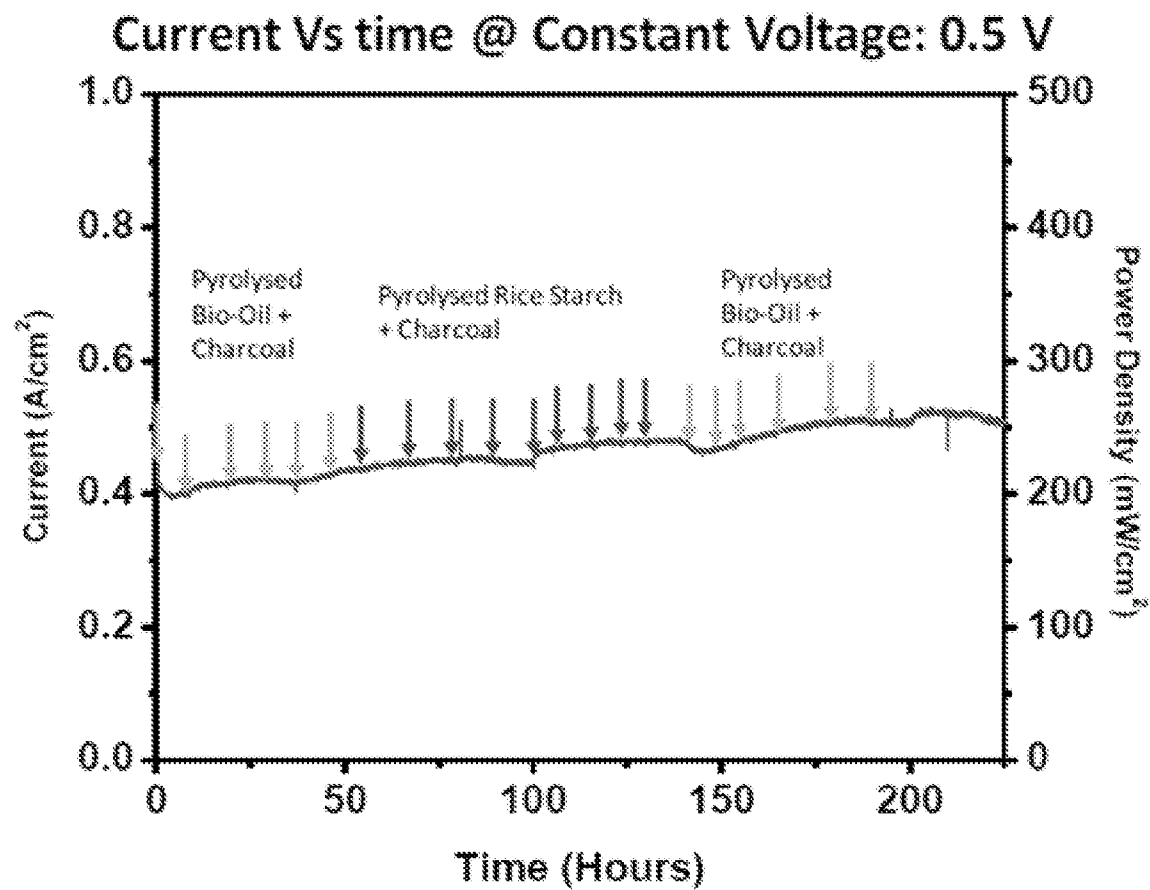
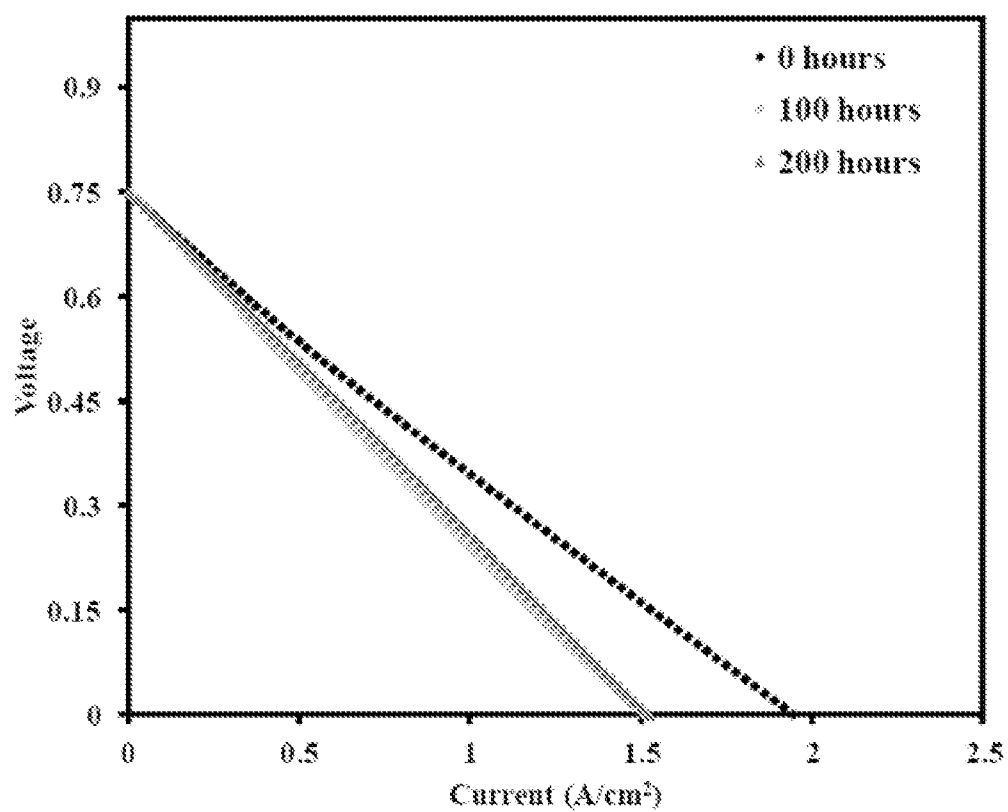


FIG. 9



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 14/30287

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01M 8/06 (2014.01)

USPC - 429/409

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)

USPC - 429/409

IPC(8) - H01M 8/06 (2014.01)

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

USPC (429/409; 429/400; 429/450; 429/451; 429/405; 429/403; 429/408; 429/104; 429/495; 429/496; 429/497; 429/505; 429/523; 429/480; 429/507; 429/513; 429/430) IPC(8) - H01M 8/06 (2014.01) (keyword delimited)

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

PatBase, Google Patents/Scholar; Search Terms Used: solid-oxide-fuel-cell direct-carbon SOFC anode cathode molten columnar fuel hydrocarbon circulate fluid-communication lead antimony density buoyancy oxidize reduce reservoir non-porous negative positive electrode liquid pipe tube passage channel storage tank chamber vessel container contact melt

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y --- A	US 2006/0234098 A1 (GUR) 19 October 2006 (19.10.2006), para [0015], [0025], [0030]-[0032], [0056], [0079]; figure 4; claim 12	1-5, 7, 11-14 ----- 28
Y --- A	US 2003/0143440 A1 (TAO et al.) 31 July 2003 (31.07.2003), para [0059], [0069], [0158]	1-5, 7, 11-14 ----- 28
A	US 2009/0117429 A1 (ZILLMER et al.) 07 May 2009 (07.05.2009), entire document, especially para [0016], [0018], [0034], [0035]; Fig 1, 2	28
A	WO 2013/019958 A1 (CALO et al.) 07 February 2013 (07.02.2013), pg 9, ln 1-4; pg 10, ln 3-18	28
A	US 6,379,828 B1 (WORTH) 30 April 2002 (30.04.2002), col 3, ln 33-44	1-5, 7, 11-14, 28
A	US 2009/0035620 A1 (FINNERTY et al.) 05 February 2009 (05.02.2009), entire document	1-5, 7, 11-14, 28

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

03 July 2014 (03.07.2014)

Date of mailing of the international search report

- 30 JUL 2014

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 14/30287

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 6, 8-10, 15-27, 29, 30
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.