

## ELECTROCHEMICAL OXIDATION OF CARBONACEOUS DEPOSITS IN LIQUID-HYDROCARBON FUELED SOLID OXIDE FUEL CELLS

### CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of priority of U.S. Patent Application No. 14/623,884 filed February 17, 2015, entitled, “Enhanced Electrochemical Oxidation of Carbonaceous Deposits In Liquid-Hydrocarbon Fueled Solid Oxide Fuel Cells” (Docket SA 6011 PA), the contents of which are hereby incorporated by reference in its entirety.

### BACKGROUND

#### *Field*

[0002] Embodiments of the present disclosure generally relate to solid oxide fuel cells (SOFCs) and, more specifically relate to a method of removing carbonaceous deposits in a liquid-hydrocarbon fueled solid oxide fuel cell and associated specially configured liquid-hydrocarbon fueled solid oxide fuel cell system.

#### *Technical Background*

[0003] As is conventionally known, a solid oxide fuel cell consists of three major parts; an anode, where electrochemical oxidation takes place, a cathode, where electrochemical reduction takes place and the electrolyte membrane, which is a dense, gas impermeable, ion transport membrane which exhibits purely ionic or mixed ionic-electronic conductivity at an elevated temperature range. Cathodes produce oxygen ions which then migrate through the electrolyte membranes to the anode electrode. The oxygen ions oxidize the fuel in the anode and thereby produce electrons, which flow through an external electrical circuit back to the cathode, thereby generating electrical energy.

[0004] Referring to FIG. 1, conventional solid oxide fuel cells **100** (SOFC), include an anode **120**. The anode **120** is in contact with the solid oxide electrolyte **170** and may also be exposed to fuel (gas, liquid or solid), for example, a carbonaceous fuel **142**. In the cathode **130**, which performs O<sub>2</sub> (g) reduction of the cathode metal in the presence of air **144** to yield oxygen ions **146**, is placed on the opposing side of the solid oxide electrolyte **170**. For current collection at the anode **120**, a metal wire, or any other electron conducting material that is solid and inert at

the operating conditions, may be electrically connected to the anode **120** to facilitate collection of the electrons which travel back to the cathode **130** via electrical circuit **150**.

[0005] Referring again to FIG. 1, an electrochemical reaction converts fuel **142** and air **144** into electricity without combustion. A solid oxide fuel cell **100** is a high temperature fuel cell. At high temperature, warmed air **144** enters the solid oxide fuel cell **100** adjacent the cathode **130** and carbonaceous fuel **142** enters the solid oxide fuel cell **100** adjacent to the anode **120**. Subsequently, a chemical reaction begins in the solid oxide fuel cell **100**. As the fuel **142** crosses the anode **120**, it attracts oxygen ions **146** from the cathode **130**. The oxygen ions **146** combine with the fuel **142** to produce electricity and waste products **148** including water, and small amounts of carbon dioxide. As long as there is fuel **142**, air **144**, and heat, the process continues producing electricity. However, as the solid oxide fuel cell **100** operates the efficiency and/or power output diminishes over time.

[0006] Accordingly, ongoing needs exist for methods of improving the long-term efficiency and power output of solid oxide fuel cells **100** and for solid oxide fuel cell systems which maintain efficiency and power output over time.

## SUMMARY

[0007] The method and systems of the present disclosure have industrial applicability, specifically in the Oil & Gas and Power industries due to the rapidly increasing worldwide energy consumption and the decreased efficiency of fuel cells over time as a result of carbonaceous deposits **140** on the anode **120**. Carbonaceous deposits **140** can build up on the anode **120** which reduces the operating efficiency of the solid oxide fuel cell **100**.

[0008] According to one embodiment, a method of removing carbonaceous deposits in a liquid-hydrocarbon fueled solid oxide fuel cell is provided. The method includes providing a solid oxide fuel cell system having an anode, a cathode, a solid oxide electrolyte oriented between the anode and cathode, an amplifier cathode disposed proximate the solid oxide electrolyte and the cathode, a fuel cell electric circuit electrically connecting the anode and the cathode, and an amplifier electric circuit electrically connecting the anode and the amplifier cathode. The method further includes operating the amplifier electric circuit in an electrolytic mode to electrically power the amplifier cathode. Operating the amplifier electric circuit in an electrolytic mode results in the amplifier cathode generating and supplying  $O^{2-}$  or  $CO_3^{2-}$  to the

anode. Further, the method includes removing the carbonaceous deposits on the anode by converting the carbonaceous deposits to carbon dioxide gas via reaction with the  $O^{2-}$  or  $CO_3^{2-}$  and expelling the carbon dioxide gas.

**[0009]** In a further embodiment, a method of removing carbonaceous deposits in a liquid-hydrocarbon fueled solid oxide fuel cell is provided. The method includes providing a solid oxide fuel cell system having an anode, a cathode, a solid oxide electrolyte oriented between the anode and cathode, an amplifier cathode disposed proximate the solid oxide electrolyte and the cathode, a fuel cell electric circuit electrically connecting the anode and the cathode, and an amplifier electric circuit comprising at least one battery, potentiostat, or galvanostat electrically connecting the anode and the amplifier cathode. Further, the method includes monitoring a power reaction speed of the solid oxide fuel cell system. The method additionally includes operating the amplifier electric circuit in an electrolytic mode to electrically power the amplifier cathode, wherein the amplifier cathode generates and supplies  $O^{2-}$  or  $CO_3^{2-}$  to the anode. Further, the method includes removing the carbonaceous deposits on the anode by converting the carbonaceous deposits to carbon dioxide gas via reaction with the  $O^{2-}$  or  $CO_3^{2-}$  and expelling the carbon dioxide gas. Finally the method includes adjusting the current supplied to the amplifier electric circuit to obtain steady-state operation of the removal of the carbonaceous deposits on the anode.

**[0010]** In yet a further embodiment, a solid oxide fuel cell system is provided. The solid oxide fuel cell system includes an anode, a cathode, a solid oxide electrolyte oriented between the anode and cathode, and an amplifier cathode disposed proximate the solid oxide electrolyte and the cathode. The solid oxide fuel cell system additionally has a fuel cell electric circuit electrically connecting the anode and the cathode and an amplifier electric circuit having at least one battery, potentiostat, or galvanostat electrically connecting the anode and the amplifier cathode. Additionally, the solid oxide fuel cell system has a liquid fuel atomizer located to distribute the liquid-hydrocarbon fuel across the anode. The amplifier electric circuit operates in an electrolytic mode to electrically power the amplifier cathode which generates and supplies  $O^{2-}$  or  $CO_3^{2-}$  to the anode to remove carbonaceous deposits on the anode by converting the carbonaceous deposits to carbon dioxide gas via reaction with the  $O^{2-}$  or  $CO_3^{2-}$  to produce carbon dioxide gas.

[0011] Additional features and advantages of the embodiments described herein will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the embodiments described herein, including the detailed description which follows, the claims, as well as the appended drawings.

[0012] It is to be understood that both the foregoing general description and the following detailed description describe various embodiments and are intended to provide an overview or framework for understanding the nature and character of the claimed subject matter. The accompanying drawings are included to provide a further understanding of the various embodiments, and are incorporated into and constitute a part of this specification. The drawings illustrate the various embodiments described herein, and together with the description serve to explain the principles and operations of the claimed subject matter.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0013] FIG. 1 is a schematic illustration of a conventional SOFC.

[0014] FIG. 2 is a schematic illustration of a SOFC with an amplifier electrical circuit in accordance with one or more embodiments of the present disclosure.

[0015] FIG. 3 depicts a SOFC system with an amplifier electrical circuit and a liquid fuel atomizer in accordance with one or more embodiments of the present disclosure.

#### **DETAILED DESCRIPTION**

[0016] Reference will now be made in detail to embodiments of the method of removing carbonaceous deposits in a liquid-hydrocarbon fueled solid oxide fuel cell and related system of the present disclosure. Though the schematics and system of FIGS. 2 and 3 are provided as exemplary, it should be understood that the present systems and methods encompass other configurations.

[0017] Referring to the embodiment of FIG. 2, a solid oxide fuel cell (SOFC) system **110** is shown. The solid oxide fuel cell system **110** comprises an anode **120**, a cathode **130**, a solid oxide electrolyte **170** oriented between the anode **120** and cathode **130**. Additionally, the solid oxide fuel cell system **110** comprises an amplifier cathode **160** disposed proximate the solid

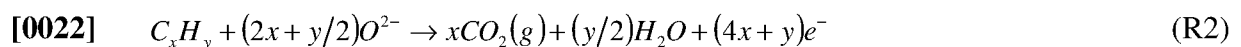
oxide electrolyte **170** and the cathode **130**. A fuel cell electric circuit **150** electrically connects the anode **120** and the cathode **130**. The solid oxide fuel cell system **110** also comprises an amplifier electric circuit **180** electrically connecting the anode **120** and the amplifier cathode **160**. As used herein, “between” does not necessarily mean directly contacting, and contemplates that additional components are suitable between the anode **120**, cathode **130**, or electrolyte **170** of the solid oxide fuel cell system **110**.

[0018] As shown in FIG. 2, the solid oxide fuel cell system **110** comprises one or more external electric circuits, for example the fuel cell electric circuit **150**, which collect electrons from the anode **120** to generate electricity. In various embodiments, the fuel cell electric circuit **150** may comprise a wire, or any other electron conducting material that is solid and inert at the operating conditions, to facilitate collection of the electrons which travel back to the cathode **130** via the fuel cell electric circuit **150**.

[0019] In operation as shown in FIG. 2, the cathode **130** reduces the O<sub>2</sub> in the inlet air stream **144** in accordance with the following reaction (R1) to generate oxygen ions **146**:



[0021] After the oxygen ions **146** migrate through the solid oxide electrolyte **170**, the oxygen ions **146** arrive at the anode **120** and oxidize the fuel **142** to produce carbon dioxide and water in addition to electrons, which are used to generate electricity. This electrochemical oxidation reaction (R2) is shown below:

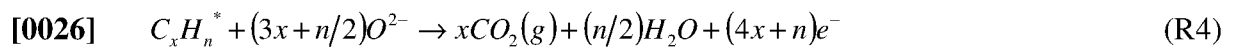


[0023] In operation, the solid oxide fuel cell system **110**, as well as the conventional solid oxide fuel cell **100**, does not operate perfectly in accordance with R2. Oxygen ions **146** are driven from the cathode **130** to the anode **120** through the solid oxide electrolyte **170**, to oxidize the fuel **142** and produce electricity. The driving force for oxygen ions **146** is a spontaneous migration as a result of the oxygen chemical potential difference between the anode **120** and cathode **130**. However, due to homogenous gas phase pyrolysis and/or cracking reactions that take place at high temperatures, carbonaceous deposits **140** are formed on the surface of the anode **120**, thereby blocking the normal operation of the anode **120** and thus deteriorate the performance of the solid oxide fuel cell **110**. Thus, carbonaceous deposits **140** build up on the

anode **120** which reduces the operational efficiency of the solid oxide fuel cell system **110**. The efficiency of the solid oxide fuel cell system **110** is the useful power generated as a percentage of the total power anticipated. The efficiency of the solid oxide fuel cell system **110** can be expressed by the formula:  $\varepsilon = P_{\text{gen}} / \Delta G_{\text{fuel}}$ , where  $\varepsilon$  is the fuel cell efficiency,  $P_{\text{gen}}$  is the useful power output and  $\Delta G_{\text{fuel}}$  the Gibbs free energy of the fuel oxidation reaction. Specifically, the accumulation of carbonaceous deposits **140** on the anode **120** occurs in accordance with the electrochemical reaction (R3) shown below.



[0025] The accumulation of the carbonaceous deposits **140** on the anode **120** is remedied by providing additional ionic oxygen **146** to the anode **120**. When the oxygen ions **146** reach the surface of the anode **120** they selectively react with the carbonaceous deposits **140** at the proximity of the triple phase boundaries (tpb) to form  $CO_2$  (g). The reaction of the carbonaceous deposits **140** and oxygen ions **146** to form  $CO_2$  results in removal of the carbonaceous deposits **140**. The reaction (R4) to remove the carbonaceous deposits **140** is provided below.



[0027] As shown in FIGS. 2 and 3, the solid oxide fuel cell system **110** comprises one or more external electric circuits in addition to the fuel cell electric circuit **150**, for example the amplifier electric circuit **180**, which operate in an electrolytic mode. Operation in an electrolytic mode means the circuit is provided power to complete electrolysis or supply power to drive an oxidation-reduction reaction in a direction in which it does not occur spontaneously. Specifically, the amplifier electric circuit **180** consumes electric energy in order to generate oxygen ions **146** at the cathode **130** for passage to the surface of the anode **120**. In various embodiments, the amplifier electric circuit **180** may comprise a wire, or any other electron conducting material that is solid and inert at the operating conditions, to facilitate transmission of electrons to the cathode **130** via the amplifier electric circuit **180**.

[0028] Operating the amplifier electric circuit **180** in an electrolytic mode electrically powers the amplifier cathode **160**. The electric powering of the amplifier cathode **160** generates and supplies  $O^{2-}$  to the anode **120**. The supplied  $O^{2-}$  as ionic oxygen **146** passing through the solid oxide electrolyte **170** removes the carbonaceous deposits **140** on the anode **120** by converting

the carbonaceous deposits **140** to carbon dioxide gas **148** via reaction with the ionic oxygen **146**. The generated carbon dioxide gas **148** is then expelled from the solid oxide fuel cell **110**. The carbon dioxide gas **148** is expelled from the solid oxide fuel cell **110** in accordance with any method known to one having skill in the art. For example, as shown in FIG. 3, piping may be utilized to direct the carbon dioxide gas **148** away from the solid oxide fuel cell **110**. In embodiments there is no need for any additional equipment to remove the produced carbon dioxide gas **148** as the pressure drop due to the carbon dioxide gas **148** flux along the pipeline is a sufficient driving force for carbon dioxide gas **148** removal.

[0029] The amplifier electric circuit **180** of the solid oxide fuel cell **110** comprises at least one power source **182** that powers the amplifier electric circuit **180**. In one embodiment, the power source **182** is at least one battery. Non-limiting examples of batteries include lithium batteries, alkaline batteries, silver-oxide batteries, zinc-carbon batteries, lead-acid batteries, lithium-ion batteries, nickel hydrogen batteries, and sodium-ion batteries. The batteries may be primary cells (non-rechargeable batteries) or secondary cells (rechargeable batteries) in various embodiments. In further embodiments, the at least one battery may be recharged by diverting a portion of the electricity produced by the solid oxide fuel cell system **110** to the battery. One having skill in the art would understand that additional specific batteries or alternative power sources are known and appreciate that they may equally be utilized as the power source **182**.

[0030] In further embodiments, the power source **182** that powers the amplifier electric circuit **180** is a fuel cell electric circuit **150**. For example, the amplifier electric circuit **180** may include at least one potentiostat which controls the power supplied to the amplifier cathode **160** from the at least one fuel cell electric circuit **150**. Specifically, the potentiostat functions by maintaining the potential of the at least one fuel cell electric circuit **150** at a constant level by adjusting the current supplied to the amplifier electric circuit **180**. In a further example, the amplifier electric circuit **180** may include at least one galvanostat which controls the power supplied to the amplifier cathode **160** from the at least one fuel cell electric circuit **150**. The potentiostat and/or galvanostat work as power supplies to provide electron current to the amplifier cathode **160**. If a constant potential between the anode **120** and the amplifier cathode **160** is desired then the potentiostat can be used, while when a constant current between the anode **120** and the amplifier cathode **160** is preferred the galvanostat can be used. Therefore, when a constant ionic oxygen **146** supply rate is required, the galvanostat is preferable.

[0031] In various embodiments, the current supplied to the amplifier electric circuit **180** is substantially constant. In further embodiments, the current supplied to the amplifier electric circuit **180** is pulsed. Whether the current supplied to the amplifier electric circuit **180** constant or pulsed, the minimum applied potential is the O<sub>2</sub> reduction potential or the corresponding current. The O<sub>2</sub> reduction potential typically ranges from approximately 0.1V to approximately 0.5V. Specific O<sub>2</sub> reduction potentials for various solid oxide fuel cell systems **110** with differing anode **120**, cathode **130**, and/or solid oxide electrolyte **170** are known to one having ordinary skill in the art. The maximum applied potential is limited to the electrolyte reduction potential or the corresponding current. The electrolyte reduction potential typically ranges from approximately 2V to approximately 3V. Specific electrolyte reduction potentials for various solid oxide fuel cell systems **110** with differing anode **120**, cathode **130**, and/or solid oxide electrolyte **170** are known to one having ordinary skill in the art.

[0032] Referring to Figs. 2 and 3, in further embodiments, the solid oxide fuel cell system **110** further comprises a voltmeter unit **156** and an ammeter unit **152** that measure the voltage and the current respectively in the fuel cell electric circuit **150**. From the measurements of the voltmeter unit **156** and the ammeter unit **152**, the power output can be simply and directly calculated.

[0033] In further embodiments, the solid oxide fuel cell system **110** further comprises a control circuit to pulse the current supplied to the amplifier electric circuit **180** as the solid oxide fuel cell's power output drops below a certain percentage of the initial non-carbon poisoned power output. The decrease in fuel cell power output before initiation of the control circuit to pulse the current supplied to the amplifier electrode circuit may be approximately 20%, approximately 30%, approximately 40%, approximately 50%, approximately 60%, approximately 70%, approximately 80%, or approximately 90% in various embodiments. Additionally, in various embodiments, the potentiostat and/or galvanostat used to apply potential or current to the amplifier circuit, may have an integrated voltmeter and ammeter to measure the voltage and current. Thus, power supplied may be simply and directly calculated.

[0034] In various embodiments, the power reaction speed of the solid oxide fuel cell system **110** is monitored. The power reaction speed may be monitored by observing the current

supplied by the fuel cell electric circuit **150** or the voltage provided by the fuel cell electric circuit **150** for example.

[0035] In various embodiments, the current supplied to the amplifier electric circuit **180** is adjusted to obtain steady-state operation of the removal of the carbonaceous deposits **140** on the anode **120**. Steady-state operation of the removal of the carbonaceous deposits **140** means the carbonaceous deposits **140** are removed at a rate equal to the rate that the carbonaceous deposits **140** form. If the carbonaceous deposits **140** are forming at a rate in excess of the rate at which the carbonaceous deposits **140** are removed, the power reaction speed of the solid oxide fuel cell system **110** decreases and the current supplied to the amplifier electric circuit **180** is increased to increase the rate of removal of the carbonaceous deposits **140**. The current supplied to the amplifier electric circuit **180** may be decreased to decrease the rate of removal of the carbonaceous deposits **140** until the rate of formation of the carbonaceous deposits **140** once again exceeds the rate of removal of the carbonaceous deposits **140**. Minimizing the current supplied to the amplifier electric circuit **180** while still removing the carbonaceous deposits **140** at a rate equal to the rate of formation of the carbonaceous deposits **140** maximizes the efficiency of the solid oxide fuel cell system **110** by avoiding unnecessary ionic oxygen **146** formation.

[0036] In various embodiments, the anode **120** is contemplated as comprising any of various metals suitable for oxidation, for example, a metallic, metal oxide, or ceramic-metallic. For example, and not by way of limitation, the anode **120** comprises metal selected from the group consisting of iron (Fe), copper (Cu), nickel (Ni), cobalt (Co), gold (Au), ruthenium (Ru), rhodium (Rh), tungsten (W), chromium (Cr), terbium (Tb), magnesium (Mg), platinum (Pt), palladium (Pd), and combinations thereof.

[0037] For the case of the solid oxide electrolyte **170**, high ionic conductivity and negligible chemical interactions with the anode **120** are required. That being said, various compositions are suitable for the solid oxide electrolyte **170**, with the major requirement being oxygen ion conductivity. Suitable solid oxide electrolytes **170** may be either purely ionic or mixed ionic-electronic.

[0038] For example, and not by way of limitation, the solid oxide electrolyte **170** may comprise zirconia based electrolytes or ceria based electrolytes. In specific embodiments, the

zirconia-based electrolyte may be selected from the group consisting of yttria stabilized  $\text{ZrO}_2$  (YSZ), scandia stabilized  $\text{ZrO}_2$  (ScSZ), calcia stabilized  $\text{ZrO}_2$  (CSZ), samaria stabilized  $\text{ZrO}_2$  (SmSZ), and combinations thereof. In an exemplary embodiment, the solid oxide electrolyte **170** comprises yttria stabilized  $\text{ZrO}_2$  (YSZ). Alternatively, the ceria-based electrolytes may comprise rare earth doped ceria. For example, the ceria-based electrolytes are selected from the group consisting of gadolinium doped ceria (GDC), yttria doped ceria (YDC), samarium doped ceria (SmDC), scandium doped ceria (ScDC), zirconium doped ceria (ZDC), gadolinia stabilized ceria (CGO) and combinations thereof. Further examples of the solid oxide electrolyte **170** include titania-based, perovskite oxides, or cationic carbonate-based electrolytes.

**[0039]** When selecting the composition for the solid oxide electrolyte **170**, the following factors should be considered: 1. any possible chemical interactions with any of the electrodes, which may have a catastrophic effect on the solid oxide fuel cell **110**; 2. the fuel cell operating temperature range; and 3. the ionic/electronic conductivity ratio value. As a result, combinations of two or more solid oxide electrolytes **170** may be used to ensure these factors are met. For example, in cases where a non-stable solid oxide electrolyte **170** (which interacts with the anode **120**) is necessary to be used in the solid oxide fuel cell **110** due to its remarkable ionic conductivity at the desired operating temperature, a thin coating of a chemically stable solid electrolyte may be used at the electrolyte/anode interface to avoid direct contact between the anode **120** and the solid oxide electrolyte **170**. The same technique can be used to block the electronic conductivity that a highly conductive mixed ionic-electronic solid electrolyte may exhibit at the desired temperature range. In that instance, a thin coating of a purely ionic conductor (e.g. YSZ) may be beneficial.

**[0040]** Regarding the cathode **130** and amplifier cathode **160**, any cathodic material that exhibits low  $\text{O}_2$  (g) reduction overpotential at the operating temperature range while having negligible interactions with the solid oxide electrolyte **170** could be used in the cathode **130** and the amplifier cathode **160**. For example and not by way of limitation, the cathode **130** or the amplifier cathode **160** may comprise of perovskite materials of the general type  $\text{ABO}_3$  or  $\text{ABMO}_3$  or  $\text{A}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$  or  $\text{A}_{1-x}\text{B}_x\text{M}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ , where A may be one of the group La, Sn, Nd, Gd, Ba or Dy; B may be one of the  $2^+$ ,  $3^+$ ,  $4^+$  or  $5^+$  cations, and M may be a transition metal. Two preferred perovskite cathodes are  $\text{LaSrFeCoO}_{3-\delta}$  (LSCF) and  $\text{LaSrMnO}_{3-\delta}$  (LSM). A further exemplary perovskite cathode is  $\text{Sr}_2\text{MgMo}_{0.8}\text{Nb}_{0.2}\text{O}_{6-\delta}$ . Additionally, transition metal

electrodes may be used as the cathode **130** or the amplifier cathode **160**. Non-limiting examples include Pt, Ir and Au.

[0041] In another embodiment, the cathode **130** and the amplifier cathode **160** are the same compositions. As the function of the cathode **130** and the amplifier cathode **160** is the same in that O<sub>2</sub> reduction occurs in both the cathode **130** and the amplifier cathode **160**, the same material can be used providing the advantage of lower overall manufacturing cost.

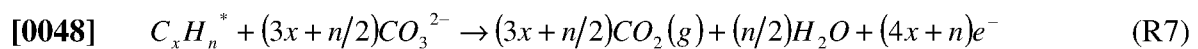
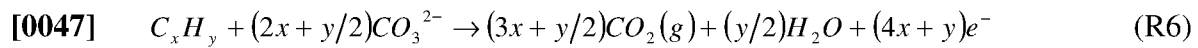
[0042] In further embodiments, the cathode **130** and the amplifier cathode **160** are different compositions. Utilizing different compositions for the cathode **130** and the amplifier cathode **160** allows high performing cathode materials which are typically more expensive to be used as the amplifier cathode **160** due to the relatively smaller size of the amplifier cathode **160** compared to the cathode **130**. Utilizing a high performing cathode material for the amplifier cathode **160** results in higher oxygen reduction rates than with a lower cost and lower performing cathode material which may compensate for the smaller size of the amplifier cathode **160**.

[0043] Referring to FIG. 3, in embodiments, the solid oxide fuel cell system **110** further comprises a liquid fuel atomizer **190**. The liquid fuel atomizer **190** is placed spaced away from the top of the anode **120**. Utilizing the liquid fuel atomizer **190** allows distribution of the fuel **142** across the anode **120**. Distribution of the fuel **142** across the anode **120** results in increased fuel utilization. Additionally, distribution of the fuel **142** across the anode **120** results in highly dispersed carbonaceous deposits **140**. The ionic oxygen **146** generated at the amplifier cathode **160** dispersed across the anode **120** as it passes through the solid oxide electrolyte **170** and thus highly dispersed carbonaceous deposits **140** are preferred to effectively utilize all the generated ionic oxygen **146**.

[0044] While not shown, several conventional (e.g. utilizing the wasted heat from a furnace), non-conventional (i.e. renewable: solar photovoltaic (PV) or concentrated solar power (CSP), wind power, etc.), or combined heating methods can be used to achieve the required high operating temperature range of the solid oxide fuel cell **110**.

[0045] In further embodiments, the fuel cell is a molten-carbonate fuel cell (MCFC). When the fuel cell is a molten-carbonate fuel cell the ionic species transferred through the solid oxide

electrolyte **170** is ionic carbonate ( $\text{CO}_3^{2-}$ ). Additionally, equations R1, R2, and R4 are replaced with R5, R6, and R7 reproduced below.



**[0049]** Liquid hydrocarbon-powered fuel cells can exhibit operation efficiency values up to 90% but the operation of direct-feed of the hydrocarbon fuel **142** at the anode **120**, where high efficiency values can be achieved, is still challenging and difficult to be applied due to the traditional issues with carbonaceous deposits **140** forming on the anode **120**. However, by removing carbonaceous deposits **140** from the anode **120** the operating efficiency of the solid oxide fuel cell system **110** is maintained. In another embodiment, the efficiency of the solid oxide fuel cell system **110** exceeds 40% and is maintained in excess of 40% indefinitely during operation of the solid oxide fuel cell system **110**. In further embodiments, the efficiency of the solid oxide fuel cell system **110** exceeds 60% and is maintained in excess of 60% indefinitely during operation of the solid oxide fuel cell system **110**. In yet even further embodiments, the efficiency of the solid oxide fuel cell system **110** exceeds 80% and is maintained in excess of 80% indefinitely during operation of the solid oxide fuel cell system **110**.

**[0050]** It should be apparent to those skilled in the art that various modifications and variations can be made to the embodiments described herein without departing from the spirit and scope of the claimed subject matter. Thus it is intended that the specification cover the modifications and variations of the various embodiments described herein provided such modification and variations come within the scope of the appended claims and their equivalents.

Claims

1. A method of removing carbonaceous deposits in a liquid-hydrocarbon fueled solid oxide fuel cell, the method comprising:

5 providing a solid oxide fuel cell system comprising an anode, a cathode, a solid oxide electrolyte oriented between the anode and cathode, an amplifier cathode disposed proximate the solid oxide electrolyte and the cathode, a fuel cell electric circuit electrically connecting the anode and the cathode, and an amplifier electric circuit electrically connecting the anode and the amplifier cathode;

10 operating the amplifier electric circuit in an electrolytic mode to electrically power the amplifier cathode, wherein the amplifier cathode generates and supplies  $O^{2-}$  or  $CO_3^{2-}$  to the anode; and

removing the carbonaceous deposits on the anode by converting the carbonaceous deposits to carbon dioxide gas via reaction with the  $O^{2-}$  or  $CO_3^{2-}$  and expelling the carbon dioxide gas.

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2. The method of claim 1, wherein the amplifier electric circuit further comprises at least one battery that powers the amplifier electric circuit.

20 3. The method of claim 1, wherein the cathode and the amplifier cathode are different compositions.

4. The method of claim 1, wherein the cathode, the amplifier cathode, or both is selected from the group consisting of at least one perovskite material of the general type  $ABO_3$  or  $ABMO_3$  or  $A_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$  or  $A_{1-x}B_xM_{1-y}Mg_yO_{3-\delta}$ , wherein:

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A is La, Sn, Nd, Gd, Ba or Dy,

B is a  $2^+$ ,  $3^+$ ,  $4^+$  or  $5^+$  cation;

and preferably wherein the perovskite material is  $LaSrFeCoO_{3-\delta}$  (LSCF), or  $LaSrMnO_{3-\delta}$  (LSM), or  $Sr_2MgMo_{0.8}Nb_{0.2}O_{6-\delta}$ .

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5. The method of claim 1, wherein the anode comprises metal selected from the group consisting of iron (Fe), copper (Cu), nickel (Ni), cobalt (Co),

molybdenum (Mo), gold (Au), ruthenium (Ru), rhodium (Rh), tungsten (W), chromium (Cr), terbium (Tb), magnesium (Mg), platinum (Pt), palladium (Pd), and combinations thereof.

5           6.       The method of claim 1, wherein the electrolyte is zirconia-based, ceria-based, titania-based, a perovskite oxide, or cationic carbonate-based.

              7.       The method of claim 1, wherein the solid oxide fuel cell system further comprises a liquid fuel atomizer located to distribute the liquid-hydrocarbon fuel across  
10   the anode.

              8.       A method according to claim 1, comprising:  
              providing a solid oxide fuel cell system comprising an anode, a cathode, a solid oxide electrolyte oriented between the anode and cathode, an amplifier cathode  
15   disposed proximate the solid oxide electrolyte and the cathode, a fuel cell electric circuit electrically connecting the anode and the cathode, and an amplifier electric circuit comprising at least one battery, potentiostat, or galvanostat electrically connecting the anode and the amplifier cathode;

              monitoring a power reaction speed of the solid oxide fuel cell system;  
20       operating the amplifier electric circuit in an electrolytic mode to electrically power the amplifier cathode, wherein the amplifier cathode generates and supplies  $O^{2-}$  or  $CO_3^{2-}$  to the anode;

              removing the carbonaceous deposits on the anode by converting the carbonaceous deposits to carbon dioxide gas via reaction with the  $O^{2-}$  or  $CO_3^{2-}$  and  
25   expelling the carbon dioxide gas; and

              adjusting the current supplied to the amplifier electric circuit to obtain steady-state operation of the removal of the carbonaceous deposits on the anode.

              9.       The method of claim 1 or claim 8, wherein the amplifier electric circuit  
30   further comprises at least one potentiostat that powers and controls the amplifier electric circuit.

10. The method of claim 1 or claim 8, wherein the amplifier electric circuit further comprises at least one galvanostat that powers and controls the amplifier electric circuit.

5 11. The method of claim 1 or claim 8, wherein the current supplied to the amplifier electric circuit is substantially constant over time.

12. The method of claim 11, wherein the current supplied to the amplifier electric circuit maintains a voltage above the O<sub>2</sub> reduction potential and below the  
10 electrolyte reduction potential.

13. The method of claim 1 or claim 8, wherein the current supplied to the amplifier electrode circuit is pulsed.

14. The method of claim 13, wherein the solid oxide fuel cell system further comprises a control circuit to pulse the current supplied to the amplifier electrode circuit such that current is supplied when the power output of the solid oxide fuel cell system drops below 50% of initial operation without carbonaceous deposits.

15. A solid oxide fuel cell system comprising:  
an anode,  
a cathode,  
a solid oxide electrolyte oriented between the anode and cathode, an amplifier cathode disposed proximate the solid oxide electrolyte and the cathode,  
25 a fuel cell electric circuit electrically connecting the anode and the cathode,  
an amplifier electric circuit electrically connecting the anode and the amplifier cathode; and

a liquid fuel atomizer located to distribute the liquid-hydrocarbon fuel across the anode, wherein the amplifier electric circuit operates in an electrolytic mode to  
30 electrically power the amplifier cathode which generates and supplies O<sup>2-</sup> or CO<sub>3</sub><sup>2-</sup> to the anode to remove carbonaceous deposits on the anode by converting the

carbonaceous deposits to carbon dioxide gas via reaction with the  $\text{O}^{2-}$  or  $\text{CO}_3^{2-}$  to produce carbon dioxide gas.