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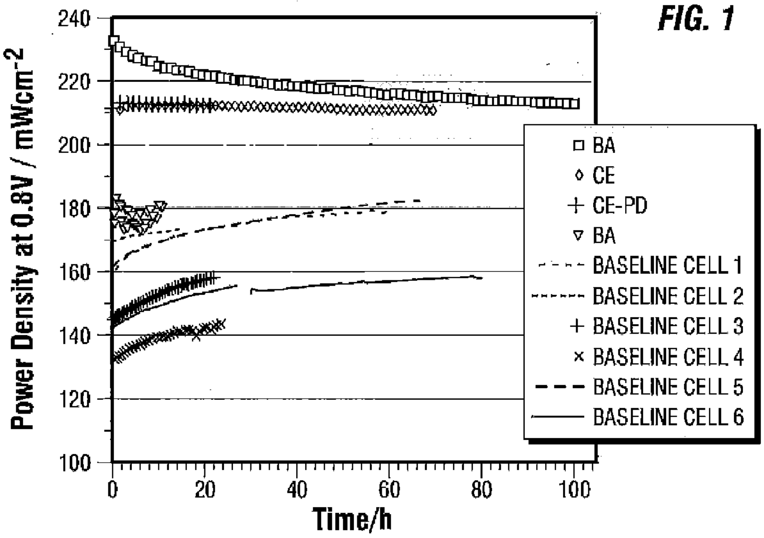

FIG. 1

(57) Abstract: A solid oxide fuel cell comprising an electrolyte, an anode and a cathode. In this fuel cell at least one electrode has been modified with a promoter using liquid phase infiltration.

LIQUID PHASE MODIFICATION OF ELECTRODES OF SOLID OXIDE FUEL CELLS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a PCT International application which claims the benefit of and priority to U.S. Provisional Application Ser. No. 61/888,229 filed October 8, 2013 and U.S. Patent Application Serial No. 14/505,958 filed October 3, 2014, entitled "Liquid Phase Modification of Solid Oxide Fuel Cells," both of which are hereby incorporated by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] None.

FIELD OF THE INVENTION

[0003] A method of liquid phase modification of solid oxide fuel cells.

BACKGROUND OF THE INVENTION

[0004] The world relies heavily on energy produced from fossil fuels, but as a non-renewable energy source (at least in our lifetimes), fossil fuels have serious limitations. The ever-increasing demand and dwindling supply of fossil fuels will inevitably cause significant problems in the future. In remote areas of developing countries, transmission and distribution of fossil fuel-generated energy can be difficult and expensive. Additionally, the burning of fossil fuels results in the formation of smog and global warming, and further contributes to our environmental problems. Thus, developing a clean alternative energy industry is key to improving the quality of life for individuals and communities, and to ameliorate global warming and other environmental problems.

[0005] The critical technical barrier to the widespread application of various alternative energy technologies is performance limitations of the key materials. For example, in solar-fuel production, the efficiency is relatively low since the current photocathode materials show sluggish H_2 evolution reaction kinetics and the photoanode materials have insufficient light absorption and carrier collection capabilities. In wind power, the lifetime of turbine blades currently made of polymer-matrix composite materials reinforced with fiberglass or graphite fibers can be further enhanced when a new material with adequate stiffness to prevent failure as well as sufficient long term fatigue in harsh conditions is developed. Therefore, materials science and technology plays a pivotal role in building the world's energy future, from fundamental discovery science, to improving energy production processes. The discovery and optimization of new materials could effectively advance solutions to our energy challenges.

[0006] The demand for clean, secure, and renewable energy has stimulated great interest in fuel cells. Fuel cells are one distinct category of devices that are capable of converting chemical energy into electrical energy. Among the fuel cells that are currently under active development, alkaline, polymeric-electrolyte-membrane and phosphoric-acid fuel cells all require essentially pure hydrogen as the fuel to be fed to the anode.

[0007] Solid Oxide Fuel Cells ("SOFCs"), on the other hand, are a type of fuel cells that use a solid oxide or ceramic as the electrolyte of a cell. The basic solid oxide fuel cell is generally made up of three layers. A single cell consisting of these three layers stacked together is typically less than a few millimeters thick. Hundreds of these cells are then connected in series to form what most people refer to as an "SOFC stack". The ceramics used in SOFCs do not become electrically and ionically active until they reach very high temperature and as a consequence the stacks have to run at temperatures ranging from 500 to 1,000°C. Reduction of oxygen into oxygen ions occurs at the cathode. These ions can then diffuse through the solid oxide electrolyte to the anode where they can electrochemically oxidize the fuel. In this reaction, a water byproduct is given off as well as two electrons. These electrons then flow through an external circuit where they can do work. The cycle then repeats as those electrons enter the cathode material again.

[0008] SOFCs offer great promise for the most efficient and cost-effective utilization of a wide variety of fuels such as hydrocarbons, coal gas and gasified biomass. Because of the relatively high operating temperature (500-1000°C), the fuel processing reaction can be carried out within the cell stacks without additional fuel processors. Another advantage of SOFCs is the fuel flexibility. A wide variety of practical hydrocarbons such as methane, propane, gasoline, diesel and kerosene can be directly utilized as the fuels in SOFCs. The direct utilization of hydrocarbon fuels will increase the operating efficiency and reduce system costs, which will accelerate substantially the use of SOFCs in transportation, residential and distributed-power application. Among the hydrocarbon fuels, natural gas such as methane is regarded as relatively cheap and popularly available fuel with plenty of deposits. Additionally, SOFCs that can directly run on natural gas would highly reduce the operating cost and accelerate the commercialization of SOFC system.

[0009] The basic chemical reactions at the anode side of an SOFC is the oxidation of fuels, such as hydrogen gas and/or carbon monoxide, to generate electrons:

Anode: $H_2 + O^{2-} \rightarrow H_2O + 2\ e^-$

and/or $CO + O^{2-} \rightarrow CO_2 + 2\ e^-$

[0010] The reaction at the cathode side is the reduction of oxygen to oxygen ions:

Cathode: $O_2 + 4e^- \rightarrow 2\ O^{2-}$

[0011] Therefore, the overall reaction of an SOFC becomes:

Overall: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

Or $H_2 + CO + O_2 \rightarrow H_2O + CO_2$

[0012] Therefore, SOFCs typically run on pure hydrogen or mixture of hydrogen and carbon monoxide by internally or externally reforming a hydrocarbon fuel, while air serves as the oxidant. As shown above, if pure hydrogen is used, then the product is pure water, whereas carbon dioxide is produced if carbon monoxide is also used. Carbon dioxide and water are produced is hydrocarbon fuels are used.

[0013] In an effort to reduce fuel electrode manufacturing costs, sintering processes have been attempted, such as those described in U.S. Pat. Nos. 4,971,830, 5,035,962, 5,908,713 and 6,248,468. However, fuel electrodes applied by a sintering process are relatively time consuming in that it still requires at least two processing steps, an initial application followed by high temperature sintering. Moreover, sintered fuel electrodes may experience marginal physical stability over time.

[0014] Other attempts to reduce fuel electrode fabrication costs include plasma spraying (e.g. atmospheric plasma spraying "APS", vacuum plasma spraying "VPS", plasma arc spraying, flame spraying) which generally involves spraying a molten powdered metal or metal oxide onto an underlying substrate surface using a plasma thermal spray gun to form a deposited layer having a microstructure generally characterized by accumulated molten particle splats. Plasma spraying techniques are described in U.S. Pat. Nos. 3,220,068, 3,839,618, 4,049,841, and U.S. Pat. Nos. 3,823,302 and 4,609,562 generally teach plasma spray guns and use thereof, each of which are herein incorporated by reference in their entirety. Although plasma spraying has been used for fabrication of certain fuel cell layers, such as those described in U.S. Pat. Nos. 5,085,742, 5,085,742, 5,234,722 5,527,633 (plasma sprayed electrolyte) U.S. Pat. No. 5,426,003 (plasma sprayed interconnect), U.S. Pat. No. 5,516,597 (plasma sprayed interlayer) and U.S. Pat. No. 5,716,422 (plasma sprayed air electrode), use of such plasma spraying techniques have been of limited value when used to apply a fuel electrode onto an electrolyte because they tend to result in a fuel electrode that poorly adheres to the electrolyte and exhibits poor thermal cyclability due to the mismatch of thermal coefficients of expansion between the metal portion of the fuel electrode and the ceramic electrolyte. Moreover, these conventional plasma spraying techniques tends to result in a fuel electrode that has a low porosity after continued use, thereby causing voltage loss when current flows as a result of polarization due to a low rate of diffusion of fuel gases into and reaction product out from the interface between the fuel electrode and electrolyte.

[0015] There is thus a need for a SOFC and a method for making the SOFC that can generally achieve above-described favorable technical properties and can be manufactured at a low cost.

BRIEF SUMMARY OF THE DISCLOSURE

[0016] A solid oxide fuel cell comprising an electrolyte, an anode and a cathode. In this fuel cell at least one electrode has been modified with a promoter using liquid phase infiltration.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] A more complete understanding of the present invention and benefits thereof may be acquired by referring to the follow description taken in conjunction with the accompanying drawings in which:

[0018] Figure 1 depicts a comparison of power density versus time.

[0019] Figure 2 depicts a comparison of fuel cell exhaust versus time.

[0020] Figure 3 depicts a comparison of fuel cell exhaust versus time.

[0021] Figure 4 depicts different power densities of cathodes.

[0022] Figure 5 depicts different power densities over time.

DETAILED DESCRIPTION

[0023] Turning now to the detailed description of the preferred arrangement or arrangements of the present invention, it should be understood that the inventive features and concepts may be manifested in other arrangements and that the scope of the invention is not limited to the embodiments described or illustrated. The scope of the invention is intended only to be limited by the scope of the claims that follow.

[0024] The current embodiments describe a solid oxide fuel cell (SOFC) comprising an electrolyte, an anode and a cathode. In this SOFC at least one electrode has been modified with a promoter using liquid phase infiltration.

[0025] In one embodiment of the SOFC the anode is typically porous to allow the fuel to flow towards the electrolyte. Anodes are typically chosen for their (1) high electrical conductivity; (2) a thermal expansion that matches those of the adjoining components; (3) the capacity to avoid coke deposition; (4) fine particle size; (5) chemical compatibility with another cell components (electrolyte and interconnector) under a reducing atmosphere at the operating temperature; (6) large triple phase boundary; (7) high electrochemical or catalytic activity for the oxidation of the selected fuel gas; (8) high porosity (20 - 40 %) adequate for the fuel supply and the reaction product removal; (9) good electronic and ionic conductive phases and (10) good catalytic activity for hydrocarbon reforming. In the current SOFC any known anode electrodes can be utilized. Types of anodes that can be used include Ni/YSZ, Cu/Ni, perovskite structures with a general formula of ABO_3. In the perovskite structure the A cations can be group 2, 3, or 10 elements or more specifically cations such as Ba, La, Sr, Ca or Sm. Also in the perovskite structure the B cations can be group 4, 6, 7, 8, 9, or 10 elements or more specifically cations such as Ti, Cr, Ni, Fe, Co, Mn or Zr. . Other materials that the anode could be include nickel oxide, nickel, yittria stabilized zirconia, scandia stabilized zirconia, gadolinium doped ceria, samarium doped ceria, doped barium zirconate cerate, or combinations thereof.

[0026] In one embodiment the anode can be pre-reduced at a temperature from about 400°C to about 800°C in a reducing atmosphere containing 1-100% hydrogen or other reducing gas atmospheres.

[0027] In one embodiment of the SOFC the cathode is typically porous to allow the oxygen reduction to occur. Any cathode material known to those skilled in the art can be used. One example of cathode materials that are typically used include perovskite-type oxides with a general formula of ABO_3. In this embodiment the A cations are typically rare earths doped with alkaline earth metals including La, Sr, Ca, Pr or Ba. The B cations can be metals such as Ti, Cr, Ni, Fe, Co, Cu or Mn. Examples of these perovskite-type oxides include $LaMnO_3$. In one differing embodiment the perovskite can be doped with a group 2 element such as Sr^{2+} or Ca^{2+}. In another embodiment cathodes such as $Pr_{0.5}Sr_{0.5}FeO_3$; $Sr_{0.9}Ce_{0.1}Fe_{0.8}Ni_{0.2}O_3$; $Sr_{0.8}Ce_{0.1}Fe_{0.7}Co_{0.3}O_3$; $LaNi_{0.6}Fe_{0.4}O_3$; $Pr_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_3$; $Pr_{0.7}Sr_{0.3}Co_{0.2}Mn_{0.8}O_3$; $Pr_{0.8}Sr_{0.2}FeO_3$; $Pr_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$; $Pr_{0.4}Sr_{0.6}Co_{0.8}Fe_{0.2}O_3$; $Pr_{0.7}Sr_{0.3}Co_{0.9}Cu_{0.1}O_3$; $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$; $Sm_{0.5}Sr_{0.5}CoO_3$; or $LaNi_{0.6}Fe_{0.4}O_3$ can be utilized. . Other materials that the cathode could be include lanthanum strontium iron cobalt oxide, doped ceria, strontium samarium cobalt oxide, lanthanum strontium iron oxide, lanthanum strontium cobalt oxide, barium strontium cobalt iron oxide, or combinations thereof.

[0028] The electrolyte used in the SOFC is responsible for conducting ions between the electrodes, for the separation of the reacting gases, for the internal electronic conduction blocking, and for forcing the electrons to flow through the external circuit. Some of the typical characteristics that electrolytes typically invoke include (1) an oxide-ion conductivity greater than 10^{-3} $S.cm^{-1}$ at the operating temperature; (2) negligible electronic conduction, which means an electronic transport number close to one; (3) high density to promote gas impermeability; (4) thermodynamic stability over a wide range of temperature and oxygen partial pressure; (5) thermal expansion compatible with that of the electrodes and other cell materials from ambient temperature to cell operating temperature; (6) suitable mechanical properties, with fracture resistance greater than 100 MPa at room temperature; (7) negligible chemical interaction with electrode materials under operation and fabrication conditions to avoid formation of blocking interface phases; (8) ability to be elaborated as thin layers (less than 30 μm) and (9) low cost of starting materials and fabrication.

[0029] In the current SOFC the electrolyte can be any electrolyte known to those skilled in the art. In one embodiment the electrolyte comprises a porous BZCYYb as the backbone and carbonate as the secondary phase within the pores of.

[0030] The weight ratio of BZCYYb in the composite electrolyte may vary, as long as the composite electrolyte can reach higher conductivity as well as current density as compared to non-composite electrolyte. In one embodiment, the weight ratio of BZCYYb in the composite electrolyte ranges from 9:1 to 1:1, but more preferably ranges from 50-90% or 70-80%. In another embodiment, the weight ratio of BZCYYb is about 75%.

[0031] The weight percentage of carbonate in the composite electrolyte also may vary, as long as the composite electrolyte can maintain physical integrity during operation. In one embodiment, the weight percentage of carbonate in the composite electrolyte ranges from 10 to 50wt%. In another embodiment, the weight percentage of carbonate in the composite electrolyte ranges from 20 to 30wt%, in yet another embodiment, the carbonate is about 25%.

[0032] In one example of preparing BZCYYb lithium-potassium carbonate is typically made first. Stoichiometrical amount of Li_2CO_3 and K_2CO_3 were mixed in the weight proportion of 45.8:52.5 and milled in a vibratory mill for 1 hour. The mixture was then heated to 600°C for 2 hours. The heated mixture was then quenched in air to the room temperature and ground. The resulting lithium-potassium carbonate was used later in the preparation of composite electrolyte with BZCYYb.

[0033] In one embodiment the BZCYYb powder was prepared by solid-state reaction, but other methods could also be used. Stoichiometric amounts of high-purity barium carbonate, zirconium oxide, cerium oxide, ytterbium oxide and yttrium oxide powders (all from Sigma-Aldrich® Chemicals) were mixed by ball milling in ethanol (or other easily evaporated solvent) for 24 h, followed by drying at 80°C for overnight and calcinations at 1100°C in air for 10 h. The calcinated powder was ball milled again, followed by another calcination at 1100°C in air for 10 h to produce single phase BZCYYb.

[0034] The resulted BZCYYb powder and the carbonate obtained above were mixed at weight ratio of 75:25 and thoroughly ground again for one hour. The mixture was then heated to 680°C for 60 minutes until only the carbonate melted and wet the BZCYYb grain boundaries in the mixture. Next, it was quenched (i.e. fast cooling) in air to room temperature. The quenched mixture was ground again to get the composite electrolyte powder.

[0035] In another example an alternate way of preparing BZCYYb powder can be described. In this embodiment stoichiometric amounts of high-purity barium carbonate, zirconium oxide, cerium oxide, ytterbium oxide, and yttrium oxide powders (all from Sigma-Aldrich® Chemicals) were mixed by ball milling in ethanol for 48 h, followed by drying in an oven and calcination at 1100°C in air for 10 h. The calcined powder was ball milled again, followed by another calcination at 1100°C in air for 10 h.

[0036] The CeO_2 and ZrO_2 powders with different particle sizes were used to optimize the fabrication procedures. To prepare electrolyte samples for the conductivity measurement, we pressed the calcined powders isostatically into a disk at 274.6 MPa. The green disks had a diameter of 10 mm, with a typical thickness of 1 mm. The disks were then sintered at 1500°C for 5 h in air (relative density > 96%).

[0037] In some embodiments a Sc-doped BZCY powder can be prepared. In one example of this embodiment BZCY-Sc with a nominal composition of $BaCe_{0.7}Zr_{0.1}Y_{0.1}Sc_{0.1}O_{3-\delta}$ (BZCY-Sc) was synthesized by a conventional solid state reaction (SSR) method. Stoichiometric amount of high-purity barium carbonate, zirconium oxide, cerium oxide, yttrium oxide and scandium oxide powders ($BaCO_3$: ZrO2 : CeO_2 : Y_2O_3 : Sc_2O_3 = 167.33 : 12.32 : 120.48 : 22.58 : 13.79, all from Sigma-Aldrich® Chemicals) were mixed by ball milling in ethanol for 24 hours, followed by drying at 80°C for overnight and calcinations at 1100°C in air for 10 hours. The calcined powder was ball milled again, followed by another calcination at 1100°C in air for 10 hours to produce single phase BZCY-Sc.

[0038] In the present method, the calcining step is carried out at preferably higher than 1000°C in air for 10 hours. However, the temperature and the length of calcination can vary, depending on different factors to be considered, such as the particle size chosen. The particle size of the zirconium oxide powder is preferably between 50 nm and 200 nm, and more preferably between 50 nm and 100 nm. The particle size of the cerium oxide powder is preferably between 1 μm and 20 μm, and more preferably between 5 and 10 μm.

[0039] As described above the current embodiments describe a SOFC wherein at least one electrode has been infiltrated with a promoter using liquid phase infiltration. This infiltration can occur either before the formation of the fuel cell or after the formation of the fuel cell.

[0040] In another embodiment the electrolyte can be yittria stabilized zirconia, scandia stabilized zirconia, gadolinium doped ceria, samarium doped ceria, doped barium zirconate cerate, or combinations thereof.

[0041] Different types of liquid phase infiltration can be utilized. In one embodiment the liquid phase infiltration involves capillary forces. Examples of different liquid phase infiltration techniques include ultrasonic spray coating, painting, spraying, or dip coating.

[0042] In one embodiment the promoter is selected from the group consisting of a group 1, group 2, group 4, group 6 or lanthanide elements when infiltrating the anode electrode. More specifically, the infiltration can be with the group selected from Mo, Pr, Mg, Ca, Sr, Ba, K, Ce, La, Zr Zr, Mn, Fe, Pd, Cu, Sn, Pt, Ag, Ru, Ir, Sm, Gd elements, or combinations thereof. In some embodiments the promoter can be an oxide or a hydroxide. Figure 1 depicts an increase in cell performance for a Ni-based anode that has been pre-reduced and modified with a cerium, cerium-palladium, or barium promoter. Figure 2 shows the fuel cell exhaust from a Ni-based anode that has been pre-reduced and modified with barium promoter compared to Figure 3 a baseline cell without the liquid phase anode modification. The anode with the barium modification exhibited better catalytic stability at the low steam to carbon ratio compared to the baseline cell.

[0043] In another embodiment the promoter is selected from the group consisting of a group 2, group 8, group 9, group 10, group 15 or lanthanide elements when infiltrating the cathode electrode. More specifically, the infiltration can be with the group selected from Pr, Sr, Ce, Fe, Co, La, Sm, Ni, Gd, Ca, Ba, Bi, Ga, Mg, Pt, Ag, Ru elements, or combinations thereof. In some embodiments the promoter can be an oxide or a hydroxide. Figure 4 depicts a baseline (un-modified) cathode is compared to cathodes that have been modified with a promoter. Modification of the cathode by Ce-Gd resulted in an increase in cell performance, whereas Co-Sr-Sm, Pd, and Pt modifications resulted in a decrease in performance. In Figure 5, the stability of the cells is shown. Modification of the cathode by Ce-Gd resulted in an improvement in the cathode stability compared to the baseline cell.

[0044] In one embodiment during chemical vapor deposition the promoter would be volatile element or compounds such as Ba, Mo, TiCl, or metal-organic compounds. During this liquid phase infiltration the promoter layer added to either the anode or the cathode can vary in thickness from about 1nm to 100 nm or even 1000 nm both on the surface and the interior of the electrode

[0045] The temperature of the liquid phase infiltration can occur at temperatures from about 50°C to about 300°C.

[0046] In one embodiment the SOFC infiltrated is comprises a porous BZCYYb electrolyte or a Sc-doped BZCY.

[0047] In closing, it should be noted that the discussion of any reference is not an admission that it is prior art to the present invention, especially any reference that may have a publication date after the priority date of this application. At the same time, each and every claim below is hereby incorporated into this detailed description or specification as an additional embodiment of the present invention.

[0048] Although the systems and processes described herein have been described in detail, it should be understood that various changes, substitutions, and alterations can be made without departing from the spirit and scope of the invention as defined by the following claims. Those skilled in the art may be able to study the preferred embodiments and identify other ways to practice the invention that are not exactly as described herein. It is the intent of the inventors that variations and equivalents of the invention are within the scope of the claims while the description, abstract and drawings are not to be used to limit the scope of the invention. The invention is specifically intended to be as broad as the claims below and their equivalents.

CLAIMS

1. A solid oxide fuel cell, comprising:

   an electrolyte;

   an anode; and

   a cathode,

   wherein at least one electrode has been modified with a promoter using liquid phase infiltration.

2. The solid oxide fuel cell of claim 1, wherein the liquid phase infiltration technique involves capillary forces.

3. The solid oxide fuel cell of claim 1, wherein the promoter is dispersed within a solution, slurry or sol.

4. The solid oxide fuel cell of claim 1, wherein the liquid phase infiltration technique involves ultrasonic spray coating, painting, spraying or dip coating.

5. The solid oxide fuel cell of claim 1, wherein the electrode infiltrated is the anode.

6. The solid oxide fuel cell of claim 1, wherein the electrode infiltrated is the cathode.

7. The solid oxide fuel cell of claim 1, wherein the anode is infiltrated with a promoter selected from the group consisting of Mo, Pr, Mg, Ca, Sr, Ba, K, Ce, La, Zr, Mn, Fe, Pd, Cu, Sn, Pt, Ag, Ru, Ir, Sm, Gd or combinations thereof.

8. The solid oxide fuel cell of claim 7, where the promoter is an oxide or a hydroxide.

9. The solid oxide fuel cell of claim 1, wherein the cathode is infiltrated with a promoter selected from the group consisting of Pr, Sr, Ce, Fe, Co, La, Sm, Ni, Gd, Ca, Ba, Bi, Ga, Mg, Pt, Ag, Ru or combinations thereof.

10. The solid oxide fuel cell of claim 9, where the promoter is an oxide or a hydroxide.

11. The solid oxide fuel cell of claim 1, wherein the liquid phase infiltration deposits a promoter layer from about 1nm to 100nm on the surface and the interior of the electrode.

12. The solid oxide fuel cell of claim 1, wherein the liquid phase infiltration deposits a promoter layer from about 1nm to 10nm on the surface and the interior of the electrode.

13. The solid oxide fuel cell of claim 1, wherein the infiltration occurs after the formation of the fuel cell.

14. The solid oxide fuel cell of claim 1, wherein the anode is pre-reduced at a temperature from about 400°C to about 1000°C in a reducing atmosphere containing 1-100% hydrogen or other reducing gas atmospheres.

15. The solid oxide fuel cell of claim 1, wherein the electrolyte is selected from the group comprising of: yittria stabilized zirconia, scandia stabilized zirconia, gadolinium doped ceria, samarium doped ceria, doped barium zirconate cerate, or combinations thereof.

16. The solid oxide fuel cell of claim 1, wherein the cathode is selected from the group comprising of: lanthanum strontium iron cobalt oxide, doped ceria, strontium samarium cobalt oxide, lanthanum strontium iron oxide, lanthanum strontium cobalt oxide, barium strontium cobalt iron oxide, or combinations thereof.

17. The solid oxide fuel cell of claim 1, wherein the anode is selected from the group comprising of: nickel oxide, nickel, yittria stabilized zirconia, scandia stabilized zirconia, gadolinium doped ceria, samarium doped ceria, doped barium zirconate cerate, or combinations thereof.

18. The solid oxide fuel cell of claim 1, wherein the electrolyte comprises a porous BZCYYb electrolyte.

19. The solid oxide fuel cell of claim 1, wherein the electrolyte comprises a Sc-doped BZCY.

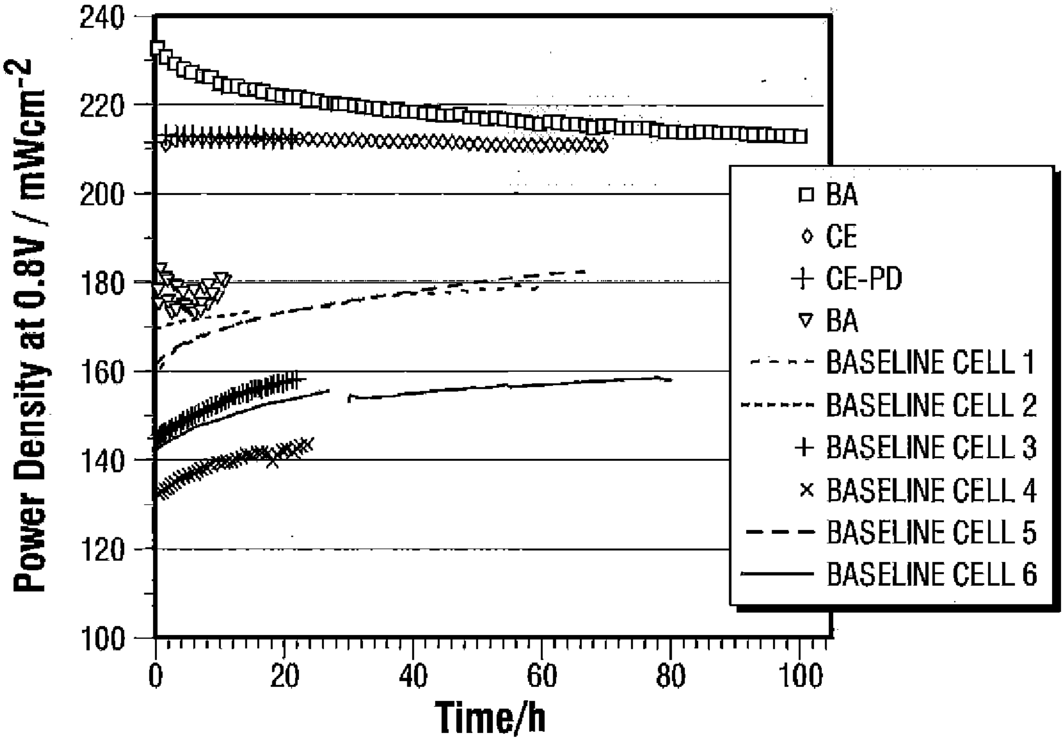
Power Density at 0.8V / mWcm-2
240
220
200
180
160
140
120
100
0
20
40
60
80
100
Time/h
□ BA
◇ CE
+ CE-PD
▽ BA
BASELINE CELL 1
BASELINE CELL 2
+ BASELINE CELL 3
× BASELINE CELL 4
BASELINE CELL 5
BASELINE CELL 6

FIG. 1

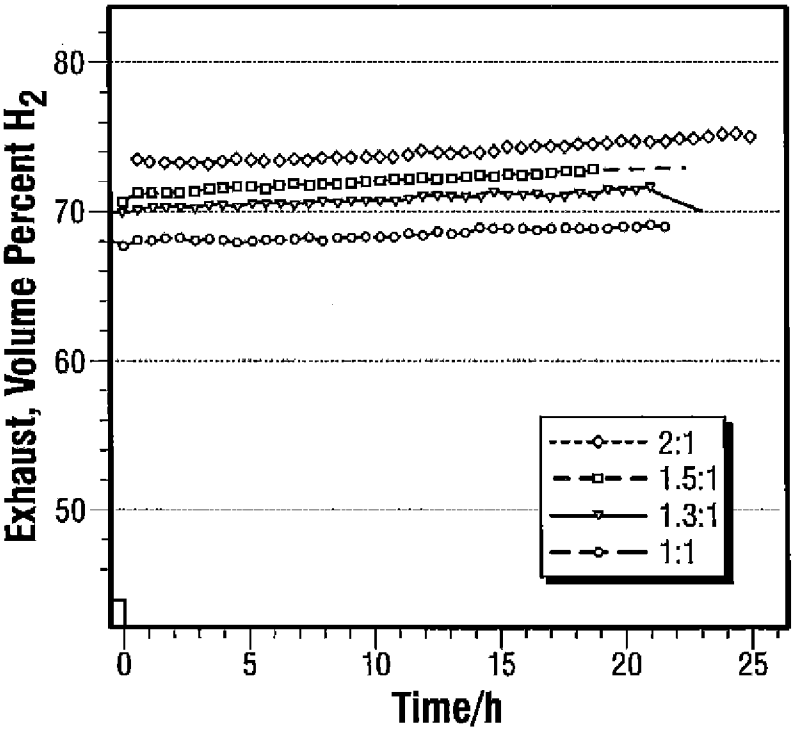
Exhaust, Volume Percent H2
80
70
60
50
0
5
10
15
20
25
Time/h
2:1
1.5:1
1.3:1
1:1

FIG. 2

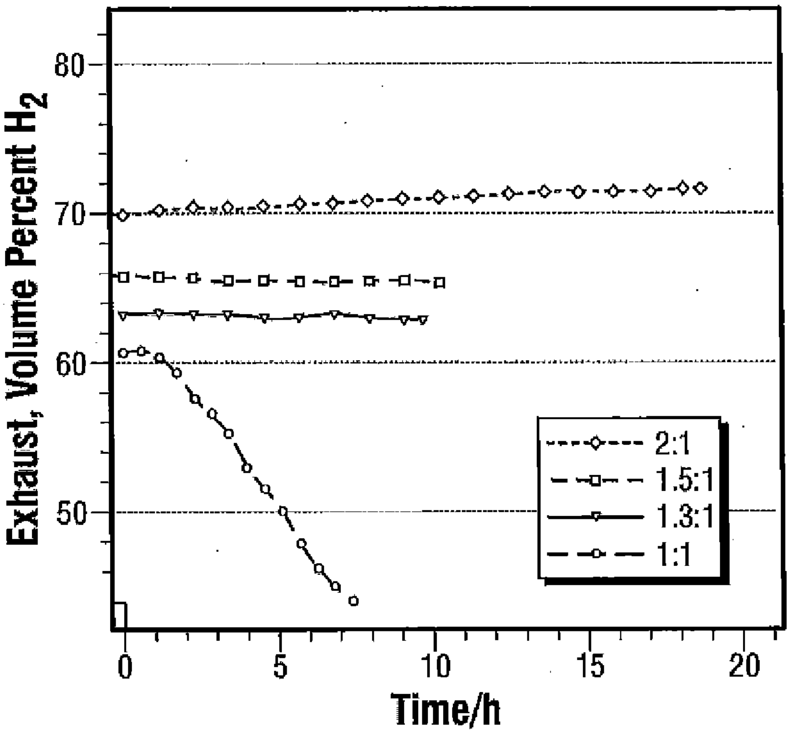
Exhaust, Volume Percent H_2
80
70
60
50
0
5
10
15
20
Time/h
2:1
1.5:1
1.3:1
1:1

FIG. 3

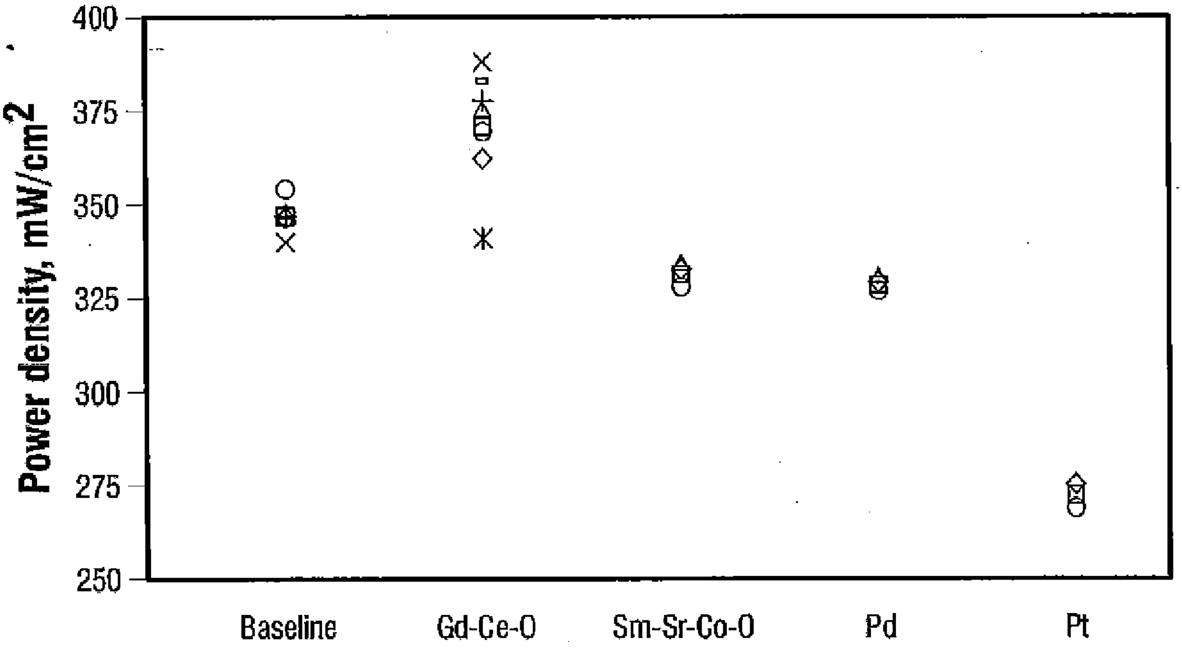
Power density, mW/cm^2
400
375
350
325
300
275
250
Baseline
Gd-Ce-O
Sm-Sr-Co-O
Pd
Pt

FIG. 4

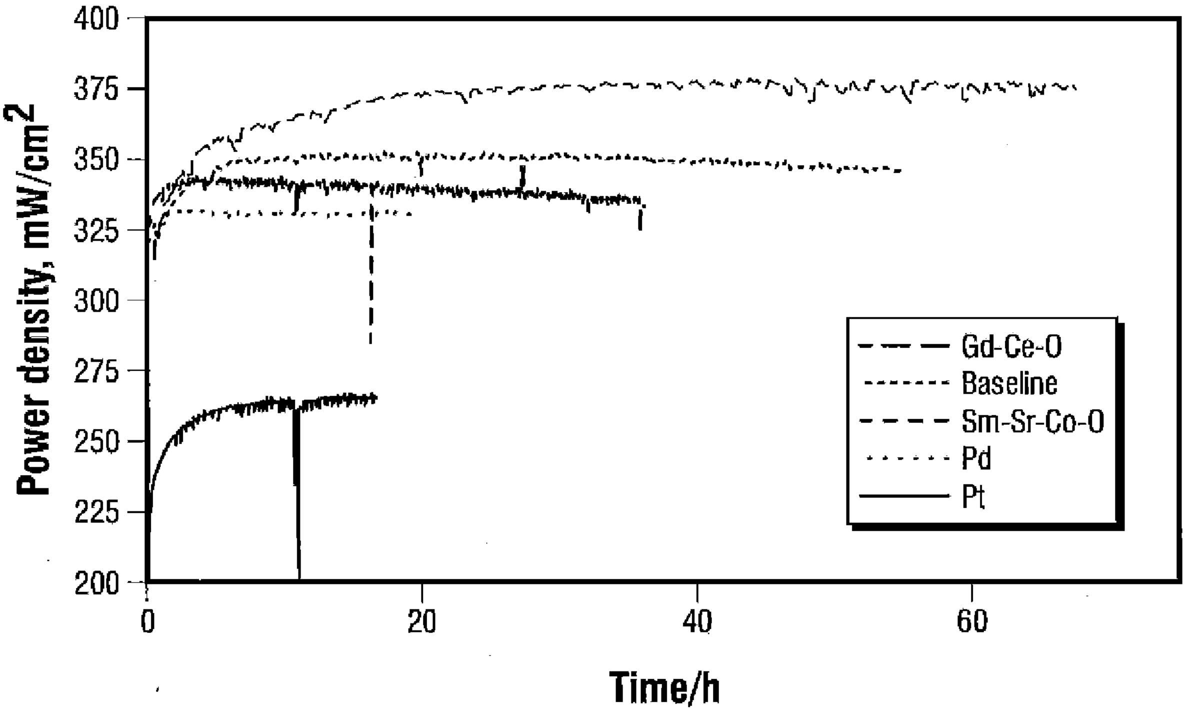
400
375
350
325
300
275
250
225
200
Power density, mW/cm²
0
20
40
60
Time/h
Gd-Ce-O
Baseline
Sm-Sr-Co-O
Pd
Pt

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/059069

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M8/12 H01M4/86 H01M4/88 H01M4/90
ADD.

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)
H01M

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 031 677 A1 (UNIV DENMARK TECH DTU [DK]) 4 March 2009 (2009-03-04)	1-4,6,9, 10,13-17
Y	abstract	18,19
A	example 18 paragraphs [0022] - [0027], [0049] - [0051] -----	11,12
X	EP 2 031 684 A2 (UNIV DENMARK TECH DTU [DK]) 4 March 2009 (2009-03-04)	1-4,6,9, 10,13-17
Y	abstract	18,19
A	examples 1-18 -----	11,12
X	EP 1 930 974 A1 (UNIV DENMARK TECH DTU [DK]) 11 June 2008 (2008-06-11)	1-4,6, 9-11, 13-17
Y	abstract paragraphs [0050] - [0056] examples 1,6 -----	18,19
	-/--	

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

☒ See patent family annex.

* Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search 3 December 2014	Date of mailing of the international search report 15/12/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Haering, Christian

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/059069

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 2012/043010 A1 (BATAWI EMAD EL [US] ET AL) 23 February 2012 (2012-02-23) abstract paragraphs [0015] - [0026]	1-5,7,8, 11,13-17 18,19
X Y A	US 2013/052562 A1 (YOON HEE SUNG [US]) 28 February 2013 (2013-02-28) abstract paragraphs [0010] - [0012]	1-5,7,8, 13-17 18,19 11,12
X Y	WO 2013/060669 A1 (UNIV DENMARK TECH DTU [DK]) 2 May 2013 (2013-05-02) abstract page 4, line 17 - page 5, line 32 page 8, line 12 - page 9, line 18; example 1	1-5,7,8, 11,13-17 18,19
Y	ELSEVIER LTD ET AL: "New ceramic material may expand uses for solid oxide fuel cells", RENEWABLE ENERGY FOCUS.COM, 1 January 2011 (2011-01-01), XP055147375, abstract	18,19
X	EP 0 439 938 A1 (WESTINGHOUSE ELECTRIC CORP [US]) 7 August 1991 (1991-08-07) cited in the application abstract; claims 1-12	1-5,7,8, 14-17

1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/059069

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.: 1-10, 14-17(all partially)
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:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
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 an 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.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-10, 14-17(all partially)

Novelty overflow

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2014/059069

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2014/059069

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