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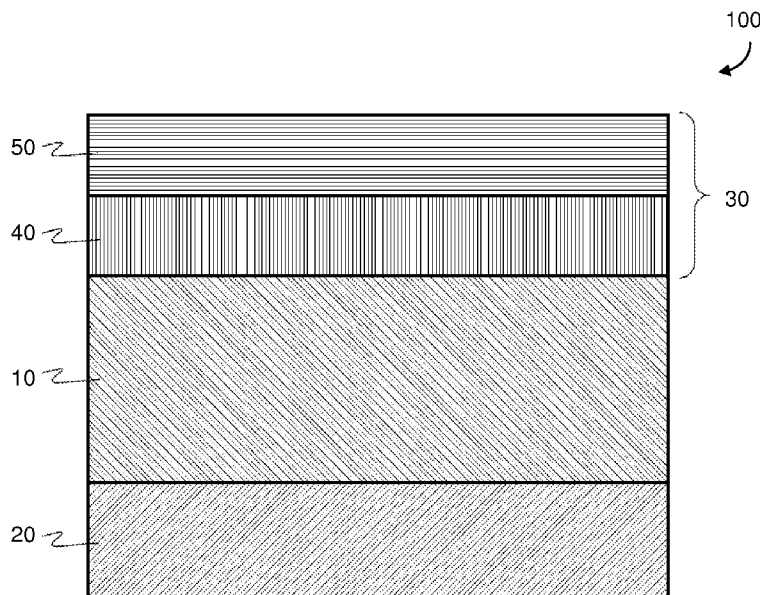
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[Continued on next page]

(54) Title: SOFC CATHODE COMPOSITIONS WITH IMPROVED RESISTANCE TO SOFC DEGRADATION



(57) Abstract: A solid oxide fuel cell (SOFC) includes a solid oxide electrolyte with a zirconia-based ceramic, an anode electrode, and a cathode electrode that includes a ceria-based ceramic component and an electrically conductive component. Another SOFC includes a solid oxide electrolyte containing a zirconia-based ceramic, an anode electrode, and a cathode electrode that includes an electrically conductive component and an ionically conductive component, in which the ionically conductive component includes a zirconia-based ceramic containing scandia and at least one of ceria, ytterbia and yttria.

FIG. 1

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SOFC CATHODE COMPOSITIONS WITH IMPROVED RESISTANCE TO SOFC DEGRADATION

CROSS REFERENCE TO RELATED PATENT APPLICATION

[0001] The instant application claims priority to U.S. Provisional Application No. 62/078,596, filed November 12, 2014 and U.S. Non-Provisional Application Serial No. 62/185,261, filed June 26, 2015, the entire contents of the applications are incorporated herein by reference.

FIELD

[0002] The present invention is generally directed to fuel cell components, and more particularly to cathode electrode materials for use in solid oxide fuel cells.

BACKGROUND

[0003] Fuel cells are electrochemical devices which can convert energy stored in fuels to electrical energy with high efficiencies. Electrolyzer cells are electrochemical devices which can use electrical energy to reduce a given material, such as water, to generate a fuel, such as hydrogen. The fuel and electrolyzer cells may comprise reversible cells which operate in both fuel cell and electrolysis mode.

[0004] In a high temperature fuel cell system, such as a solid oxide fuel cell (SOFC) system, an oxidizing flow is passed through the cathode side of the fuel cell while a fuel flow is passed through the anode side of the fuel cell. The oxidizing flow is typically air, while the fuel flow can be a hydrocarbon fuel, such as methane, natural gas, pentane, ethanol, or methanol. The fuel cell, operating at a typical temperature between 650°C and 950°C, enables the transport of negatively charged oxygen ions from the cathode flow stream to the anode flow stream, where the ion combines with either free hydrogen or hydrogen in a hydrocarbon molecule to form water vapor and/or with carbon monoxide to form carbon dioxide.

[0005] The excess electrons from the negatively charged ion are routed back to the cathode side of the fuel cell through an electrical circuit completed between anode and cathode, resulting in an electrical current flow through the circuit. A solid oxide reversible fuel cell (SORFC) system generates electrical energy and reactant product (i.e., oxidized fuel) from fuel and oxidizer in a fuel cell or discharge mode and generates the fuel and oxidant using electrical energy in an electrolysis or charge mode.

SUMMARY

[0006] A solid oxide fuel cell (SOFC) according to various embodiments is composed of a solid oxide electrolyte that includes a zirconia-based ceramic, an anode electrode, and a cathode electrode that includes a ceria-based ceramic component and an electrically conductive component. In an embodiment SOFC, the ceria-based ceramic includes at least one of samaria doped ceria (SDC), gadolinia doped ceria (GDC), and yttria doped ceria (YDC), and the solid oxide electrolyte is at least 80 wt% zirconia. In another embodiment SOFC, the electrically conductive component includes an electrically conductive ceramic selected from the group of lanthanum strontium manganite (LSM), lanthanum calcium manganite (LCM), lanthanum strontium cobalt ferrite (LSCF), lanthanum strontium ferrite (LSF), lanthanum strontium manganese ferrite (LSMF) and lanthanum strontium chromite (LSCr), and lanthanum strontium cobaltite (LSCo).

[0007] A SOFC according to other embodiments is composed of a solid oxide electrolyte that includes a zirconia-based ceramic, an anode electrode, and a cathode electrode that includes an electrically conductive component and an ionically conductive component. In some embodiments, the ionically conductive component includes a zirconia-based ceramic containing scandia and at least one of ceria, ytterbia and yttria.

[0008] In another embodiment SOFC, the cathode electrode contains around 10–90 wt% of each of the ionically conductive component and the electrically conductive

component, and the ionically conductive component includes scandia-stabilized zirconia (SSZ), ceria, and at least one of yttria and ytterbia.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIG. 1 is a cross-sectional view of a representative solid oxide fuel cell (SOFC) according to an embodiment.

[0010] FIG. 2 is a side cross sectional view of a SOFC stack according to an embodiment.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0011] A SOFC 100 generally includes an anode electrode 30, a solid oxide electrolyte 10, and a cathode electrode 20, as shown in FIG. 1. A variety of materials may be used to form the anode electrode. Example anode layer materials may include cermets that are composed of a nickel-containing phase and a ceramic phase.

[0012] The electrolyte layer in the SOFC may be composed of an ionically conductive material, such as a zirconia stabilized with scandia. Typically, zirconia is doped with between 8 and 11 mol% scandia (Sc_2O_3) in order to stabilize the cubic phase zirconia at high SOFC operating temperature of 800–850°C. In some electrolytes, the scandia stabilized zirconia is co-doped with a one or more secondary rare earth oxide, such as ceria and/or at least one of yttria and ytterbia. One example electrolyte composition is 10Sc1Ce zirconia (10 mol% Sc_2O_3 – 1 mol% CeO_2 – zirconia). Another example electrolyte composition is 10Sc1Y (10 mol% Sc_2O_3 – 1 mol% Y_2O_3 – zirconia). Another example electrolyte composition is 10Sc1Ce1Yb (10 mol% Sc_2O_3 – 1 mol% CeO_2 – 1 mol% Yb_2O_3 – zirconia).

[0013] In a SOFC in which the electrolyte layer contains a stabilized zirconia material, the cathode includes an electrically conductive material, such as one or more electrically conductive perovskite (e.g., lanthanum strontium manganite (LSM), lanthanum strontium cobaltite (LSCo), etc.) or metal (e.g., platinum). In some SOFCs, the cathode may be a mixture of the electrically conductive material and an ionically conductive material, such as scandia stabilized zirconia (SSZ).

[0014] The present inventors realized that common SOFC materials may undergo voltage degradation based, for example, on changes in electrode microstructures, reactions between materials, changes in internal material structure, and/or poisoning from impurities in fuel or oxidant gases. For example, in composite cathodes, stabilized zirconia (e.g., SSZ) forms resistive phases (i.e., “zirconates”) with cobalt- or manganese-based perovskite materials that are typically used as the electrically conductive material. This zirconate formation, which typically occurs early-on during use of the SOFC, causes voltage degradation and therefore reduces performance of the SOFC. Further, the SSZ material experiences continued ageing at the SOFC operating temperatures of 800–850°C. That is, an SSZ-containing cathode may slowly exhibit decreased conductivity over time.

[0015] The various embodiments provide improved composite cathode materials for use with zirconia-based electrolyte materials in SOFCs. In particular, embodiment SOFC cathodes may be various mixtures of ionically and electrically conductive components that are selected to avoid short term voltage degradation and long-term decrease in stability in SOFCs with zirconia-based ceramic electrolytes.

[0016] In some embodiment cathodes, the ionically conductive component may be a doped ceria-based ceramic, for example, samaria doped ceria (SDC), gadolinia doped ceria (GDC), or yttria doped ceria (YDC). For example, embodiment ceria-based ceramics compositions may have a formula of:



where A is at least one of Sm, Gd, or Y, x may be greater than 0.1 but less than or equal to 0.4. Preferably, x may be 0.5–0.4, such as x=0.2.

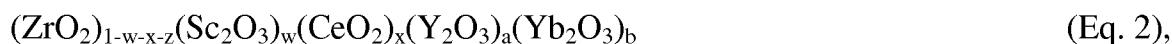
[0017] In other embodiment cathodes, the ionically conductive component may be a SSZ-based ceramic composition that also contains one or more additional stabilizing oxide (e.g., ceria, yttria, and/or ytterbia). Such additional oxide(s) may provide sufficient stabilization to the SSZ composition to reduce or prevent the ageing decomposition of the cathode. Without wishing to be bound to a particular theory, it

is believed that the stabilizing oxide provides the stabilization of the cubic phase of SSZ, thereby suppressing a cubic to tetragonal phase transformation.

[0018] Thus, the various embodiment cathodes may have either a ceria-based ceramic or SSZ-based ceramic as the ionically conductive component. In each of these embodiments, the electrically conductive component may be any of a number of electrically conductive ceramics, such as those with perovskite-based or spinel-based crystal structures. Classes of such electrically conductive ceramics may include, but are not limited to, perovskite manganites (e.g., lanthanum strontium manganite (LSM) and/or lanthanum calcium manganite (LCM)), perovskite ferrites (e.g., lanthanum strontium cobalt ferrite (LSCF), lanthanum strontium ferrite (LSF), and/or lanthanum strontium manganese ferrite (LSMF)), perovskite chromites (e.g., lanthanum strontium chromite (LSCr)), spinel magnesium cobalt oxide (MgCo_2O_4), etc. In some embodiments, the electrically conductive component may include, additionally or alternatively, various metals (e.g., platinum).

[0019] In some embodiment cathodes, the SSZ-based ceramic composition may contain SSZ and 0–3 mole percent (mol%) total of additional stabilizing oxide, such as both ceria and at least one of yttria and ytterbia.

[0020] For example, the SSZ composition may contain 0.5–2.5 mol% total of ceria and at least one of yttria and ytterbia, such as 0.9–2.1 mol% total of ceria and at least one of yttria and ytterbia. The SSZ composition may contain 0.25–1.25 mol% ceria, such as 0.4–1.1 mol% ceria, and 0.25–1.25 mol% yttria, ytterbia, or a combination of yttria and ytterbia, such as 0.4–1.1 mol% of yttria, ytterbia or a combination of yttria and ytterbia. An example SSZ-based ceramic may be 10Sc1Ce1Y (10 mol% Sc_2O_3 – 1 mol% CeO_2 – 1 mol% Y_2O_3 – zirconia). Another example SSZ-based ceramic may be 10Sc1Ce1Yb (10 mol% Sc_2O_3 – 1 mol% CeO_2 – 1 mol% Yb_2O_3 – zirconia). In some embodiments, the SSZ-based ceramic composition may contain substantially no ceria (e.g., an unavoidable trace amount of ceria or less than 0.1 mol% ceria) if the composition contains at least 0.75 mol% ytterbia, such as 1 mol% ytterbia. Thus, the SSZ-based ceramic in embodiment cathodes may have the formula:



where $0.09 \leq w \leq 0.11$, $0 < x \leq 0.0125$, $a + b = z$, and $0.0025 \leq z \leq 0.011$, and $x + z \leq 0.02$. Preferably, x ranges from 0.0025–0.0125, such as 0.004–0.011, z ranges from 0.0025–0.0125, such as 0.004–0.011, and the total of x and z is greater than or equal to 0.005 and less than or equal to 0.021, such as greater than or equal to 0.01 and less than or equal to 0.02. More preferably, $w = 0.1$, $x = 0.01$, and $z = 0.01$ for an SSZ-based ceramic, according to embodiments based on Equation 2. In other embodiments based on Equation 2, the SSZ-based ceramic and electrolyte may have the same composition, with $0.009 \leq x \leq 0.011$ and $0.009 \leq z \leq 0.011$.

[0021] Example cathode SSZ-based ceramic compositions, according to the various embodiments based on Equation 2, include:

10Sc1Ce1Y (10 mol% Sc_2O_3 + 1 mol% CeO_2 + 1 mol% Y_2O_3), remainder zirconia;
 10Sc1Ce0.5Y (10 mol% Sc_2O_3 + 1 mol% CeO_2 + 0.5 mol% Y_2O_3), remainder zirconia;
 10Sc1Ce1Yb (10 mol% Sc_2O_3 + 1 mol% CeO_2 + 1 mol% Yb_2O_3), remainder zirconia;
 10Sc1Ce0.5Yb (10 mol% Sc_2O_3 + 1 mol% CeO_2 + 0.5 mol% Yb_2O_3), remainder zirconia;
 10Sc0.5Ce0.5Y (10 mol% Sc_2O_3 + 0.5 mol% CeO_2 + 0.5 mol% Y_2O_3), remainder zirconia;
 10Sc0.5Ce0.5Yb (10 mol% Sc_2O_3 + 0.5 mol% CeO_2 + 0.5 mol% Yb_2O_3), remainder zirconia;
 10Sc0.5Ce1Y (10 mol% Sc_2O_3 + 0.5 mol% CeO_2 + 1 mol% Y_2O_3), remainder zirconia;
 10Sc0.5Ce1Yb (10 mol% Sc_2O_3 + 0.5 mol% CeO_2 + 1 mol% Yb_2O_3), remainder zirconia;
 and
 10Sc1Yb (10 mol% Sc_2O_3 + 1 mol% Yb_2O_3), remainder zirconia.

[0022] In various embodiments, the amount of scandia may be greater than the amount of ceria and the amount of the at least one of yttria and ytterbia. The amount of ceria may be equal to, less than or greater than the amount of the at least one of yttria and ytterbia.

[0023] Embodiment cathodes may be 10–90 wt% ionically conductive ceramic material and 10–90 wt% electrically conductive ceramic material, such as 25–75 wt%, and preferably 30–70 wt% of each. In some embodiments, the cathode may also contain one or more additional catalyst material (e.g., cobalt, platinum, ruthenium,

etc.) and/or sintering aid (e.g., cobalt, magnesium, nickel, iron, copper, etc.) In various embodiments, the additional one or more catalyst material and/or sintering aid may be around 0.5–5 wt% of the cathode.

[0024] The various SOFC embodiments may be utilized as the cathode layer of a planar SOFC, as illustrated in FIG. 1. In some embodiments, SOFC 100 may contain an electrolyte layer 10 that supports a cathode electrode 20 and an anode electrode 30. The cathode electrode 20 may be composed of the composite materials that include the formulas as described above. For example, the cathode electrode 20 may contain around 10–90 wt% of an ionically conductive phase, and around 10–90 wt% of an electrically conductive phase. For example, the cathode electrode 20 may contain around 55–75 wt%, preferably 70 wt%, of an ionically conductive ceramic (e.g., SDC or ScCeSZ), and around 25–45 wt%, preferably 30 wt%, of an electrically conductive ceramic (e.g., LSM).

[0025] In an alternative embodiment, the cathode electrode 20 has a graded composition where the amount of ionically conductive material decreases from the electrolyte-cathode interface towards the free surface of the cathode electrode, and/or the amount of the electrically conductive ceramic material increases from the electrolyte-cathode towards the free surface of the cathode electrode. This can be achieved in a continuous manner or in a plurality of layers varying in the ratio of the ionically conductive to the electrically conductive ceramics. Preferably, the ratio of the ionically conductive component to the electrically conductive component in the cathode electrode decreases from the electrolyte-cathode interface towards the free surface of the cathode electrode).

[0026] The electrolyte 10 may be composed of an ionically conductive phase that includes zirconia stabilized with scandia and at least one of ceria, yttria and ytterbia. In some embodiments, the electrolyte 10 material may be at least 80 wt% zirconia. In some embodiments, the composition of the electrolyte 10 may match (e.g., be the same as) that of the ionically conductive component (i.e., SSZ-containing ceramic) of certain embodiment cathodes cathode 20 in some embodiments. Compositions and

configurations of the electrolyte layer may comprise those discussed in U.S. Patent No. 8,580,456, which is hereby incorporated by reference in its entirety herein.

[0027] A method of forming the planar, electrolyte supported SOFC 100 shown in FIG. 1, includes forming the cathode electrode 20 on a first side of a planar solid oxide electrolyte 10 and forming the anode electrode 30 on a second side of the planar solid oxide electrode. The anode and the cathode may be formed in any order on the opposite sides of the electrolyte, and may be fired separately or together.

[0028] As shown in FIG. 1, the anode electrode 30 may contain one layer or a plurality of sublayers. Thus, the anode electrode 30 may optionally contain a first portion 40 and a second portion 50, each varying in composition and nickel content. For example, the first portion 40 may be located between an electrolyte 10 and the second portion 50, and may contain lower porosity compared to the second portion 50 of the anode electrode 30. The second portion 50 of the anode electrode may contain a higher ratio of the nickel containing phase to the ceramic phase than the first portion 40 of the anode electrode. Compositions, orientations and configurations of the cathode 20 and anode 30 electrodes may comprise those discussed in U.S. Patent No. 8,748,056, which is hereby incorporated by reference in its entirety.

[0029] In some embodiments, the anode 30 may be a composite anode composed of a solid oxide ionically conductive phase (e.g., SDC, GDC or YDC), and an electrically conductive phase, such as a metal (e.g., nickel, copper, cobalt, platinum, palladium, etc. or their alloys).

[0030] An embodiment method of operating a SOFC, for example, the fuel cell 100 of FIG. 1, may include operating the fuel cell 100 at 800–850°C for at least 4,000 hours in air and hydrogen-containing ambient provided on the cathode and anode side of the electrolyte, respectively. The fuel may be a hydrocarbon fuel which is reformed to hydrogen-containing fuel at the anode or upstream at an external reformer. Preferably, cathode materials of fuel cell 100 do not form resistive phases (i.e., zirconates) during the increase from room temperature to around 800–850°C, and therefore the voltage degradation of the SOFC is minimized (e.g., less than 15%).

Also, cathode materials may have a high starting ionic conductivity of 0.14 S/cm or greater, preferably 0.15 S/cm or greater (e.g., 0.16–0.17 S/cm), and preferably maintain stable conductivity after operating at 800–850°C for at least 4,000 hours. That is, in an air and/or hydrogen-containing environment, after 4,000 hours and at a temperature of 800–850°C, degradation in ionic conductivity of embodiment cathode materials be less than around 15%, such as 0–15%, for example 0–10%, including 1–5%.

[0031] The SOFC 100 is preferably an electrolyte supported cell in which the electrolyte is at least one order of magnitude thicker than the electrodes. For example, the electrolyte 10 may be about 150–300 microns thick, and the cathode electrode 20 and anode electrode 30 may each be about 10–50 microns thick, such as 20–40 microns thick. In various embodiments, the electrolyte 10 may be a planar electrolyte. The cathode 20 may be formed on one side of the planar solid oxide electrolyte 10, and the anode 30 formed on another (e.g., opposite) side of the planar solid oxide electrolyte 10. The anode and the cathode may be formed in any order on the opposite sides of the electrolyte.

[0032] Fuel cell stacks are frequently built from a plurality of SOFCs 100 in the form of planar elements, tubes, or other geometries. The stack may comprise a plurality of planar or plate shaped fuel cells. The fuel cells may have other configurations, such as tubular. The stacks may be vertically oriented stacks or the fuel cells may be stacked horizontally or in any other suitable direction between vertical and horizontal. A plurality of interconnects are located in the stack, such that each fuel cell is located between two interconnects, and each interconnect acts as a gas separator plate, as described in U.S. Application Numbers 11/907,204 and 11/785,034, each of which is incorporated by reference in its entirety herein.

[0033] FIG. 2 shows an example fuel cell stack 200, one component of which may be a so called gas flow separator (referred to as a gas flow separator plate in a planar stack) 60 that separates the individual cells in the stack. The gas flow separator plate separates fuel, such as a hydrocarbon and/or hydrogen fuel, flowing to the fuel

electrode (i.e. anode 30) of one cell in the stack from oxidant, such as air, flowing to the air electrode (i.e. cathode 20) of an adjacent cell in the stack. The separator 60 contains gas flow passages or channels 70 between the ribs 80. Frequently, the gas flow separator plate 60 is also used as an interconnect which electrically connects the fuel electrode 30 of one cell to the air electrode 20 of the adjacent cell. In this case, the gas flow separator plate which functions as an interconnect is made of or contains electrically conductive material. An electrically conductive contact layer, such as a nickel contact layer, may be provided between the anode electrode and the interconnect. In stack 200, the lower SOFC 100 is located between two gas separator plates 60.

[0034] Furthermore, while FIG. 2 shows that the stack 200 comprises a plurality of planar or plate shaped fuel cells, the fuel cells may have other configurations, such as tubular. Still further, while vertically oriented stacks are shown in FIG. 2, the fuel cells may be stacked horizontally or in any other suitable direction between vertical and horizontal.

[0035] The term “fuel cell stack,” as used herein, means a plurality of stacked fuel cells which share a common fuel inlet and exhaust passages or risers. The “fuel cell stack,” as used herein, includes a distinct electrical entity which contains two end plates which are connected to power conditioning equipment and the power (i.e., electricity) output of the stack. Thus, in some configurations, the electrical power output from such a distinct electrical entity may be separately controlled from other stacks. The term “fuel cell stack” as used herein, also includes a part of the distinct electrical entity. For example, the stacks may share the same end plates. In this case, the stacks jointly comprise a distinct electrical entity, such as a column. In this case, the electrical power output from both stacks cannot be separately controlled.

[0036] The foregoing description of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and modifications and variations are possible in light of the above teachings or may be acquired from practice of the invention. The

description was chosen in order to explain the principles of the invention and its practical application. It is intended that the scope of the invention be defined by the claims appended hereto, and their equivalents.

CLAIMS:

1. A solid oxide fuel cell (SOFC), comprising:
 - a solid oxide electrolyte comprising a zirconia-based ceramic;
 - an anode electrode; and
 - a cathode electrode comprising a ceria-based ceramic component and an electrically conductive component.
2. The SOFC of claim 1, wherein the ceria-based ceramic component comprises at least one of samaria doped ceria (SDC), gadolinia doped ceria (GDC), and yttria doped ceria (YDC), and wherein the electrolyte is at least 80 wt% zirconia.
3. The SOFC of claim 2, wherein the ceria-based ceramic component comprises a formula $Ce_{(1-x)}A_xO_2$, wherein A comprises at least one of samaria (Sm), gadolinium (Gd), and yttria (Y), wherein x is in a range of around 0.1 to 0.4, and wherein the solid oxide electrolyte comprises scandia stabilized zirconia.
4. The SOFC of claim 1, wherein the electrically conductive component comprises an electrically conductive ceramic selected from the group consisting of lanthanum strontium manganite (LSM), lanthanum calcium manganite (LCM), lanthanum strontium cobalt ferrite (LSCF), lanthanum strontium ferrite (LSF), lanthanum strontium manganese ferrite (LSMF) and lanthanum strontium chromite (LSCr), and lanthanum strontium cobaltite (LSCo).
5. The SOFC of claim 2, wherein the cathode electrode contains around 10–90 wt% of the ceria-based ceramic component and around 10–90 wt% of the electrically conductive component.
6. The SOFC of claim 5, wherein the cathode electrode contains around 55–75 wt% of the ceria-based ceramic component and around 25–45 wt% of the electrically conductive component.

7. The SOFC of claim 6, wherein the cathode electrode contains around 70 wt% of the ceria-based ceramic component and around 30 wt% of the electrically conductive component.
8. The SOFC of claim 5, wherein the cathode further comprises at least one of an additional catalyst material comprising one or more of cobalt, platinum, or ruthenium, and a sintering aid comprising one or more of cobalt, magnesium, nickel, iron, or copper.
9. The SOFC of claim 8, wherein the cathode contains less than 0.5 wt% of the at least one of the additional catalyst material and the sintering aid.
10. A solid oxide fuel cell (SOFC), comprising:
 - a solid oxide electrolyte comprising a zirconia-based ceramic;
 - an anode electrode; and
 - a cathode electrode comprising an electrically conductive component and an ionically conductive component, wherein the ionically conductive component comprises a zirconia-based ceramic containing scandia and at least one of ceria, ytterbia and yttria.
11. The SOFC of claim 10, wherein the cathode electrode contains around 10–90 wt% of each of the ionically conductive component and around 10–90 wt% of the electrically conductive component.
12. The SOFC of claim 10, wherein the ionically conductive component comprises scandia-stabilized zirconia (SSZ), ceria, and at least one of yttria and ytterbia, and wherein the solid oxide electrolyte comprises scandia stabilized zirconia.
13. The SOFC of claim 10, wherein the ionically conductive component and the solid oxide electrolyte each comprise a formula

$(\text{ZrO}_2)_{1-w-x-z}(\text{Sc}_2\text{O}_3)_w(\text{CeO}_2)_x(\text{Y}_2\text{O}_3)_a(\text{Yb}_2\text{O}_3)_b$, wherein $0.09 \leq w \leq 0.11$, $0 < x \leq 0.0125$, $a + b = z$, and $0.0025 \leq z \leq 0.0125$.

14. The SOFC of claim 13, wherein $0.009 < x \leq 0.011$, $0.009 \leq z \leq 0.011$, and wherein the ionically conductive component and the solid oxide electrolyte have the same composition.

15. The SOFC of claim 10, wherein the electrically conductive component comprises an electrically conductive ceramic selected from the group consisting of lanthanum strontium manganite (LSM), lanthanum calcium manganite (LCM), lanthanum strontium cobalt ferrite (LSCF), lanthanum strontium ferrite (LSF), lanthanum strontium manganese ferrite (LSMF) and lanthanum strontium chromite (LSCr), and lanthanum strontium cobaltite (LSCo).

16. The SOFC of claim 10, wherein the cathode electrode further comprises 0.5 wt% or less at least one of an additional catalyst material comprising one or more of cobalt, platinum, or ruthenium, and a sintering aid comprising one or more of cobalt, magnesium, nickel, iron, or copper.

17. The SOFC of claim 10, the cathode electrode has a graded composition where a ratio of the ionically conductive component to electrically conductive component in the cathode electrode decreases from an electrolyte-cathode interface towards a free surface of the cathode electrode.

18. A method of operating a solid oxide fuel cell comprising a zirconia-based electrolyte and a cathode electrode containing an electrically conductive component and an ionically conductive component, the method comprising operating the solid oxide fuel cell at 800–850°C for at least 4000 hrs such that the SOFC does not experience a voltage degradation of greater than 15%.

19. The method of claim 18, wherein the ionically conductive component comprises a ceria-doped ceramic and the electrically conductive component comprises a perovskite ceramic.

20. The method of claim 18, wherein the ionically conductive component comprises scandia-stabilized zirconia (SSZ)-based ceramic containing scandia, ceria, and at least one of ytterbia and yttria, and the electrically conductive component comprises a perovskite ceramic.

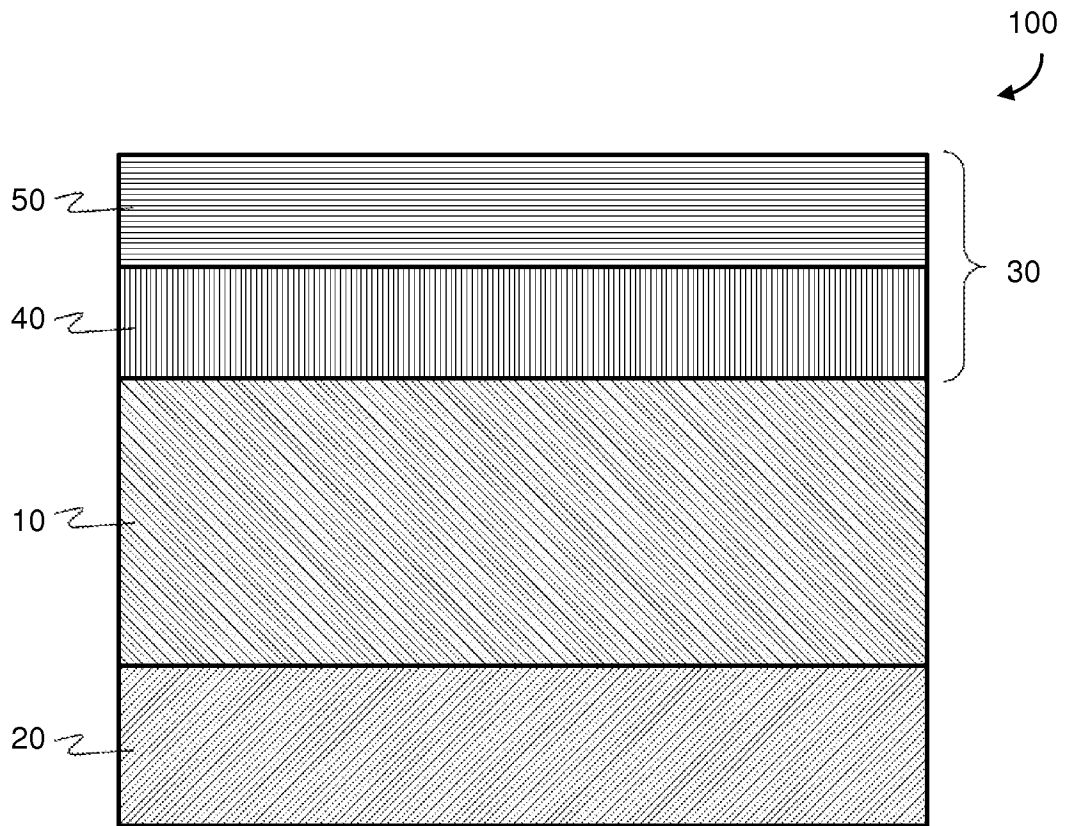


FIG. 1

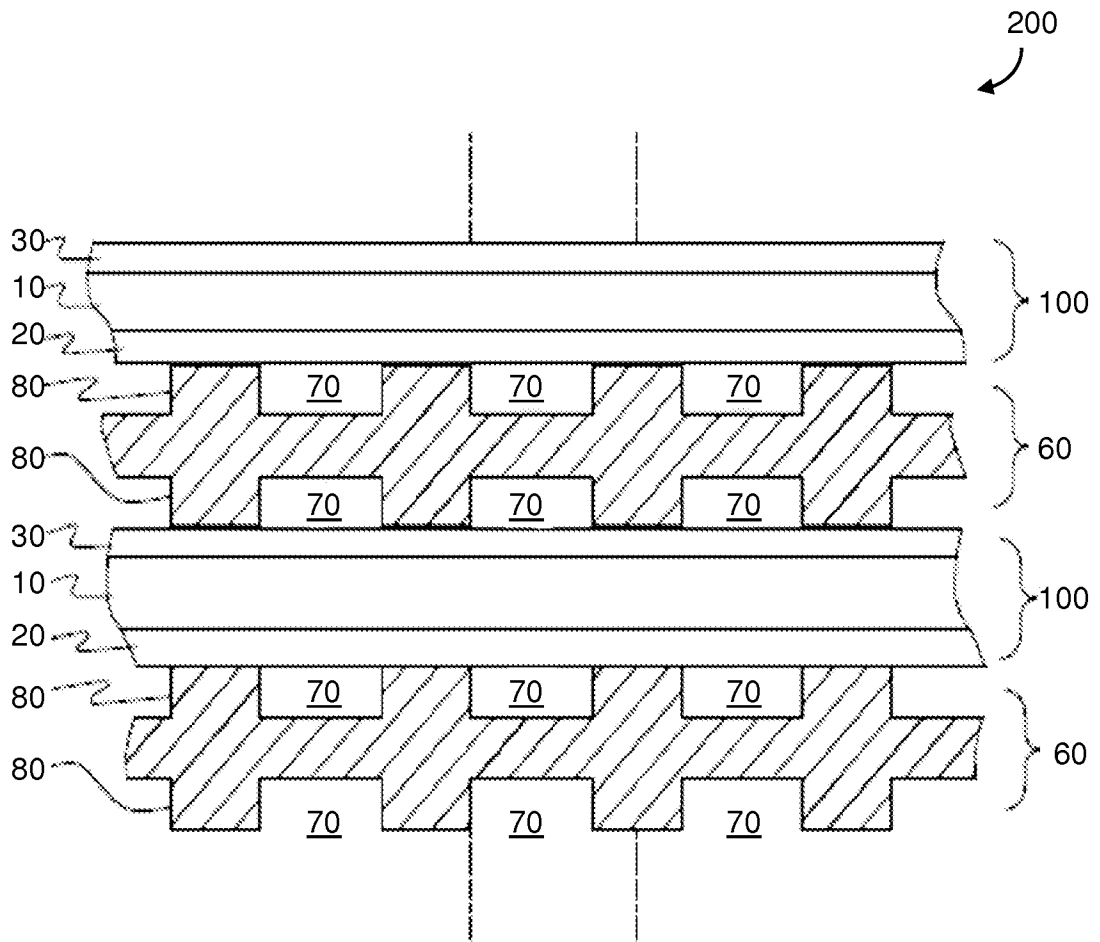


FIG. 2

A. CLASSIFICATION OF SUBJECT MATTER**H01M 8/12(2006.01)i, H01M 4/86(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHEDMinimum documentation searched (classification system followed by classification symbols)
H01M 8/12; B05D 5/12; H01M 4/90; H01M 8/10; B05D 1/00; H01M 4/64; H01M 4/86Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility modelsElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: SOFC, ceria-based, zirconia-based, GDC, LSCF, samaria, gadolinia, scandia, yttria, ytterbia, lanthanum, strontium, ionically conductive, electrically conductive, catalyst, sintering aid, voltage degradation, perovskite**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013-0295484 A1 (SAMSUNG ELECTRONICS CO., LTD.) 07 November 2013 See abstract; paragraphs [0059]-[0174]; and table 2.	1-9, 18, 19
X	US 2014-0170531 A1 (SAINT-GOBAIN CERAMICS & PLASTICS, INC.) 19 June 2014 See abstract; and paragraphs [0018]-[0070].	10-18, 20
A	US 2012-0028162 A1 (GOTTMANN, MATTHIAS et al.) 02 February 2012 See abstract; and paragraphs [0022]-[0040].	1-20
A	US 2012-0270139 A1 (PARK, HEE-JUNG et al.) 25 October 2012 See abstract; and paragraphs [0054]-[0140].	1-20
A	US 2008-0096080 A1 (BATAWI, EMAD EL et al.) 24 April 2008 See abstract; and paragraphs [0013]-[0041].	1-20

 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

29 January 2016 (29.01.2016)

Date of mailing of the international search report

29 January 2016 (29.01.2016)

Name and mailing address of the ISA/KR

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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.:
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:

I. Group 1: Claims 1-9, 18 (partially), 19 relate to a solid oxide fuel cell and a method of operating a solid oxide fuel cell, comprising a cathode electrode comprising a ceria-based ceramic component and an electrically conductive component.

II. Group 2: Claims 10-17, 18 (partially), 20 relate to a solid oxide fuel cell and a method of operating a solid oxide fuel cell, comprising a cathode electrode comprising a zirconia-based ceramic containing scandia and at least one of ceria, ytterbia and yttria.

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 any 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.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2015/059754

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