must withstand temperatures up to at least 600℃ in air or reducing environment encountered in the solid oxide fuel cells.

The interconnect materials must also be highly electrically conducting from room temperature to the operating temperatures. Few metals or metallic alloys have these properties. These include platinium, gold, osmium, iridium, and nickel based super alloys for aerospace applications. These metallic alloys are very expensive. Ceramic alloys based on mixed oxides have been developed and used successfully. Materials such as lanthanum oxide - chromium oxide have been developed for the high temperature solid oxide fuel cells. These materials are not very suited for low temperature solid oxide fuel cells operating from 400 - 600℃. Platinium and gold are suitable but simply too expensive for use in solid oxide fuel cells.

Therefore, there is a need for an improvement of interconnect material to be used in solid oxide fuel cells across temperatures.

SUMMARY OF INVENTION

Accordingly, there is provided a composition of interconnect materials for solid oxide fuel cell across temperatures, characterized in that, the materials include Iron Oxide - Copper Oxide and Ytterbium Oxide.

The present invention consists of several novel features and a combination of parts hereinafter fully described and illustrated in the accompanying description and drawings, it being understood that various changes in the details may be made without departing from the scope of the invention or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be fully understood from the detailed description given herein below and the accompanying drawings which are given by way of illustration only, and thus are not limitative of the present invention, wherein:

Figure 1 shows a graphical view of resistivity of composition 9 elevated up to 750°C in air;

Figure 2 shows a graphical magnified view of Figure 1 showing that the materials have resistivities of the order of a few ohm.m as the temperature increases from 350 °C and 600°;

Figure 3 shows a graphical view of energy gap of the materials between two temperatures;

Figure 4 shows a graphical view of a low energy gap of the semiconducting interconnect materials of the invention containing chromium oxide;

Figure 5 shows a front view of rainbow colour developed in composition with small addition of chromium oxide after short exposure in butane flame;

Figure 6 shows a graphical view of low resistivity of composition $Fe_{0.30}Cu_{0.62}Cr_{0.08}Yb_{2-x}O_{3-x}$ determined in ambient environment; and

Figure 7 shows a top view of materials of the inventions without the chromium oxide melted at 1280°C.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention relates to a composition of interconnect materials for solid oxide fuel cell across temperatures, characterized in that, the materials include Iron Oxide - Copper Oxide and Ytterbium Oxide. Hereinafter, this specification will describe the present invention according to the preferred embodiment of the present invention. However, it is to be understood that limiting the description to the preferred embodiment of the invention is

merely to facilitate discussion of the present invention and it is envisioned that those skilled in the art may devise various modifications and equivalents without departing from the scope of the appended claims.

The following detailed description of the preferred embodiment will now be described in accordance with the attached drawings, either individually or in combination.

A composition of interconnect materials for solid oxide fuel cell across temperatures is described herein. The materials include Iron Oxide - Copper Oxide and Ytterbium Oxide. The composition may also include Iron Oxide - Copper Oxide and Ytterbium Oxide with addition of Chromium Oxide up to 10 % by weight of chromium oxide.

The composition of interconnect materials are prepared by conventional and established ceramic processing routes; hence manufacturing of the materials is intrinsically very low cost. Moreover, the sintering temperatures for the ceramic materials of the invention are all below 1200℃ in air, thus can be classified as a low energy intensity process.

Table 1 discloses the various ceramic compositions studied. Of these, only 2 systems designated number 8 and 9 are found to have the required properties for interconnect materials. It is of commercial interest as the major compositions of the materials of the invention consist of iron oxide and copper oxide, both low cost and commonly available materials, with some minor phase being the rare earth oxide such as ytterbium oxide,

Table 1. Summary of various mixed oxide systems and compositions investigated for interconnect materials for solid oxide fuel cells.

Of the thirteen compositions investigated, only compositions containing Iron Oxide - Copper Oxide-Ytterbium Oxide and Iron oxide - Copper Oxide - Ytterbium Oxide - Chromium Oxide (designated No 8 and 9) have the required properties for interconnect applications, particularly for low temperature and intermediate temperature solid oxide fuel cells.

For the sintered ceramic components, in the mixed oxide state, the resistivity of the interconnect materials decreases drastically as the temperature increases as shown in Figure 1 and 2.

The resistivity approaches about 2 ohm.m or so at 600°C and rises to about 12 ohm.m at about 700°C. The nature of the drop in the electrical or resistivity with increase in temperatures indicates that the materials of the invention behaves as high temperature semiconductors up to about 600°C. The semiconducting nature of the materials of the invention is further confirmed as the resistivity is very high of the order of several hundred kilo ohms (practically insulating) at liquid nitrogen temperature.

One would expect the electrical conductivity of the mixed sintered ceramic oxide to increase as the temperature increases. Using the relation between the electrical conductivity of materials with temperature for insulators and semiconductors given by $\sigma = \sigma_o \exp - E_g/2kT$, where σ is the electrical conductivity, σ_o a parameter consisting of temperature, density of states, mobility etc., E_g the band gap between the valence and conduction band, k Boltzmann's constant, and T the temperature in Kelvin. The energy gap of the semiconducting materials of the invention is given by the slopes of log σ vs 1/T, where T is the temperature in Kelvin as shown in Figure 3.The energy gap of the materials between two temperatures has been evaluated from the slopes of the plot in Figure 3. This is depicted in Figure 4.

It can be seen that the band gap decreases from about 0.60 eV between 150C-200C down to 0.13 eV between 500C - 600C. The low band gap reflects ease with which electrical conduction can be activated.

The results show clearly that the interconnect materials of the inventions have potential for use as interconnect materials for low and intermediate temperature solid oxide fuel cells operating in the range of 400-600℃. The sharp increase in the conductivity as the temperature increase strongly suggests that the mixed sintered ceramic oxides of the invention are basically high temperature semiconductors.

The resistances of the sintered mixed oxide ceramics subjected to a reducing butane flame to simulate the service conditions of the solid oxide fuel cells have also been measured. As the surface of the materials come in contact with the reducing flame, the reduction of the copper and iron oxides presumably form some metallic phases as there is some darkening of the surfaces. This reduced materials become highly electrically conducting. Resistance of the material particularly on the surface dropped drastically almost to zero ohm as measured by a normal electrical meter. The surfaces of the reduced samples, moreover, exhibit a distinct rainbow coloration a shown in Figure 5.

It can be seen in Figure 5 that the electrical resistivity of the sintered mixed oxide ceramic, which has been heated previously up to 750^{o}C in air for several hours, increases up to around 350^{o}C; thereafter, the resistivity increases very slowly up to 700^{o}C. The resistivity is of the order of 1.0 to 3.0 ohm.m. This increase in the resistivity of the sample is attributed slight oxidation of the metallic phase(s) rather than the increase due to the temperature coefficient of resistivity of the metallic phase like copper and iron, as the resistivity of copper or iron or its alloys is of the order of 10^{-8} Ohm.m, and the temperature coefficient of resistivity α of copper and iron is of the order of 10^{-4} K^{-1}, thus the resistivity using the relation $\rho_T = \rho_o(1 + \alpha\Delta T + \beta\Delta T^2 \cdots)$ even at 700C (973K) is still of the order of 10^{-7} ohm.m.

The fact that the resistivity remains relatively constant and of the order of a few ohm.m between 350 - 700C in air further implies that the materials of the invention, have potential for use as interconnect materials in solid oxide fuel cells.

It is evident that the materials retain low resistivity when evaluated in oxidizing environment. This indicates that the materials can be used as interconnect on the cathode side where the oxidant is introduced, and also in reducing environment where the fuel such as hydrogen, or carbon based fuel is introduced.

The evidence presented in Figure 3 shows clearly that the materials of the invention behaves like a semiconductor. Such type of semiconductors, basically belong to a family of high temperature semiconductors.

In addition, it is shown that the materials, after exposed to an oxidizing environment, still retain sufficiently low electrical resistivity of the order of one or two ohm.m up to 700℃ in air. This further demonstrates that the material can be used as interconnect materials for devices such as solid oxide fuel cells operating up to 700^{o}C in air, inert and or reducing environment. The materials in particulate form can be used in the form of a paste as a low resistance contact materials for devices operating at elevated temperature up to 750^{o}C in oxidising, inert or reducing atmospheres.

The materials can be used as high temperature semiconductor sensors. Such type of devices are useful to monitor the performance of gas turbines, high intensity discharge lamps, thermoelectric generators (TEG), Magneto-Hydrodynamic Generators (MHD) and so on up to 750C and possibly much higher temperature because the materials with the addition of chromium oxide disclosed in the invention is sintered at 1280C without incurring any distortion or melting.

The materials disclosed in this invention are, further, found to be also magnetic down to liquid nitrogen temperature (77K). This is a rather surprising effect, as the copper oxide content is very high, around 45% by weight in the mixed and sintered ceramic oxide. XRD of the mixed sintered ceramic oxide exhibits sharp diffraction peaks. Preliminary analysis shows that the crystalline phase could be ytterbium iron cuprate.

The area of interest where the magnetic properties of the materials of the invention have important implications is when the cathode and anode materials are also magnetic. This magnetic nature of the interconnect materials are then attracted to the anode and the cathode thus enhancing the electrical contact and improving the reliability and performance of the solid oxide fuel cells. Since most of the anode materials consist of ferromagnetic nickel phase, and the novel cathode materials of the invention consist of iron and cobalt oxides phases, thus with ferromagnetic or ferrimagnetic properties, the conducting and magnetic properties of the materials of the interconnect materials of the invention are moreover, found to be magnetically attracted to the anode and cathode. The enhanced contact between the electrodes and the interconnect materials further enhances the reliability of the electrical contact, and performance of the devices as encountered in solid oxide fuel cells.

It is well known in the art that the anode, cathode and electrolyte must have matching thermal expansion to minimize thermal stresses, and mechanical damage of the ceramic components. Even slight mismatch in thermal expansion can be detrimental to the performance as the intimate contact at the interface may be compromised. Under such circumstances, the use of solid oxide fuel cell materials with some additional or inherent magnetic properties that encourage intimate contact with the multilayer components, are highly desirable, and should be beneficial to the performance of the devices.

The microstructures developed in the reducing butane flame is also found to be unique in the sense that after a short exposure (2 - 5 minutes) in the reducing butane flame, the surface of the materials is reduced to a metallic state, causing the materials to be attracted to cathode and anode that are also magnetic for enhanced contacts and performance of solid oxide fuel cells. The bulk inside the sample is still in the sintered mixed oxide ceramic state. We have thus produced a composite material which is metallic on the outside and non metallic in the interior. Such type of structure can be designated as topological conductor. If the surface is superconducting, the interior is semiconducting, conducting or insulating; this

is a topological superconductor. Likewise if the surface is insulating, and the interior is electrically conducting, this is basically a topological insulator. These types of materials have useful properties and numerous applications.

It is of interest to mention that the materials of the invention without the chromium oxide melt around 1050℃. This is depicted clearly in Figure 7.

The materials as can be clearly seen in Figure 7 wet a polycrystalline alumina substrate, and flow down the alumina cylinder. The materials of the invention without the chromium oxide can therefore be used as a low temperature sealing material in the planar design of the solid oxide fuel cells.

The materials of the invention with addition of chromium oxide moreover, does not show any distortion or melting even at 1280℃ in air when place on a similar alumina substrate. These materials with the chromium oxide are also electrically conducting and as disclosed can be used as interconnect materials up to 750C in oxidizing, inert and reducing environment.

It is of interest to stress that sealing material is absolutely vital to seal the components hermetically to prevent the fuel from the anode chamber mixing with the oxidant such as air or oxygen in the cathode chamber. The mixing of the fuels and the oxidant leads to serious deterioration of the anode and high likelihood of explosion when oxygen from the air or pure oxygen combines with hydrogen. Low temperature sealing materials with thermal expansion closely matching the interconnect materials, anode and cathode are therefore highly desirable.

The disclosed invention is suitable, but not restricted to, for use in low and intermediate temperature solid oxide fuel cells ranging from 350℃ to 750℃ in oxidizing as well as in reducing environment. There are potential applications in high end designer jewelries and thus valuable materials in the leisure and fashion industries. The invention can be used as high temperature semiconductor sensors up to 750℃ in air, inert and reducing environment.

must withstand temperatures up to at least 600℃ in air or reducing environment encountered in the solid oxide fuel cells.

The interconnect materials must also be highly electrically conducting from room temperature to the operating temperatures. Few metals or metallic alloys have these properties. These include platinium, gold, osmium, iridium, and nickel based super alloys for aerospace applications. These metallic alloys are very expensive. Ceramic alloys based on mixed oxides have been developed and used successfully. Materials such as lanthanum oxide - chromium oxide have been developed for the high temperature solid oxide fuel cells. These materials are not very suited for low temperature solid oxide fuel cells operating from 400 - 600℃. Platinium and gold are suitable but simply too expensive for use in solid oxide fuel cells.

Therefore, there is a need for an improvement of interconnect material to be used in solid oxide fuel cells across temperatures.

SUMMARY OF INVENTION

The invention is defined in the independent claim. Some optional features of the invention are defined in the dependent claims.

There is disclosed a composition of interconnect materials for solid oxide fuel cell across temperatures, characterized in that, the materials include Iron Oxide - Copper Oxide and Ytterbium Oxide.

The present invention consists of several novel features and a combination of parts hereinafter fully described and illustrated in the accompanying description and drawings, it being understood that various changes in the details may be made without departing from the scope of the invention or sacrificing any of the advantages of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be fully understood from the detailed description given herein below and the accompanying drawings which are given by way of illustration only, and thus are not limitative of the present invention, wherein:

Figure 1 shows a graphical view of resistivity of composition 9 elevated up to 750℃ in air;

Figure 2 shows a graphical magnified view of Figure 1 showing that the materials have resistivities of the order of a few ohm.m as the temperature increases from 350 ℃ and 600℃;

Figure 3 shows a graphical view of energy gap of the materials between two temperatures;

Figure 4 shows a graphical view of a low energy gap of the semiconducting interconnect materials containing chromium oxide;

Figure 5 shows a front view of rainbow colour developed in composition with small addition of chromium oxide after short exposure in butane flame;

Figure 6 shows a graphical view of low resistivity of composition $Fe_{0.30}Cu_{0.62}Cr_{0.08}Yb_{2-x}O_{3-x}$ determined in ambient environment; and

Figure 7 shows a top view of materials without the chromium oxide melted at 1280℃.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present disclosure relates to a composition of interconnect materials for solid oxide fuel cell across temperatures, characterized in that, the materials include Iron Oxide - Copper Oxide and Ytterbium Oxide. Hereinafter, this specification will describe the present invention according to the preferred embodiment of the present invention. However, it is to be understood that limiting the description to the preferred embodiment of the invention is

merely to facilitate discussion of the present invention and it is envisioned that those skilled in the art may devise various modifications and equivalents without departing from the scope of the appended claims.

The following detailed description of the preferred embodiment will now be described in accordance with the attached drawings, either individually or in combination.

A composition of interconnect materials for solid oxide fuel cell across temperatures is described herein. The materials include Iron Oxide - Copper Oxide and Ytterbium Oxide. The composition may also include Iron Oxide - Copper Oxide and Ytterbium Oxide with addition of Chromium Oxide up to 10 % by weight of chromium oxide.

The composition of interconnect materials are prepared by conventional and established ceramic processing routes; hence manufacturing of the materials is intrinsically very low cost. Moreover, the sintering temperatures for the ceramic materials are all below 1200℃ in air, thus can be classified as a low energy intensity process.

Table 1 discloses the various ceramic compositions studied. Of these, only 2 systems designated number 8 and 9 are found to have the required properties for interconnect materials. It is of commercial interest as the major compositions of the materials of the invention may consist of iron oxide and copper oxide, both low cost and commonly available materials, with some minor phase being the rare earth oxide such as ytterbium oxide,

Table 1. Summary of various mixed oxide systems and compositions investigated for interconnect materials for solid oxide fuel cells.

Of the thirteen compositions investigated, only compositions containing Iron Oxide - Copper Oxide-Ytterbium Oxide and Iron oxide - Copper Oxide - Ytterbium Oxide - Chromium Oxide (designated No 8 and 9) have the required properties for interconnect applications, particularly for low temperature and intermediate temperature solid oxide fuel cells.

For the sintered ceramic components, in the mixed oxide state, the resistivity of the interconnect materials decreases drastically as the temperature increases as shown in Figure 1 and 2.

The resistivity approaches about 2 ohm.m or so at 600°C and rises to about 12 ohm.m at about 700°C. The nature of the drop in the electrical or resistivity with increase in temperatures indicates that the materials behaves as high temperature semiconductors up to about 600°C. The semiconducting nature of the materials is further confirmed as the resistivity is very high of the order of several hundred kilo ohms (practically insulating) at liquid nitrogen temperature.

One would expect the electrical conductivity of the mixed sintered ceramic oxide to increase as the temperature increases. Using the relation between the electrical conductivity of materials with temperature for insulators and semiconductors given by $\sigma = \sigma_o \exp - E_g/2kT$, where σ is the electrical conductivity, σ_o a parameter consisting of temperature, density of states, mobility etc., E_g the band gap between the valence and conduction band, k Boltzmann's constant, and T the temperature in Kelvin. The energy gap of the semiconducting materials is given by the slopes of log σ vs 1/T, where T is the temperature in Kelvin as shown in Figure 3.The energy gap of the materials between two temperatures has been evaluated from the slopes of the plot in Figure 3. This is depicted in Figure 4.

It can be seen that the band gap decreases from about 0.60 eV between 150C-200C down to 0.13 eV between 500C - 600C. The low band gap reflects ease with which electrical conduction can be activated.

The results show clearly that the interconnect materials have potential for use as interconnect materials for low and intermediate temperature solid oxide fuel cells operating in the range of 400-600℃. The sharp increase in the conductivity as the temperature increase strongly suggests that the mixed sintered ceramic oxides are basically high temperature semiconductors.

The resistances of the sintered mixed oxide ceramics subjected to a reducing butane flame to simulate the service conditions of the solid oxide fuel cells have also been measured. As the surface of the materials come in contact with the reducing flame, the reduction of the copper and iron oxides presumably form some metallic phases as there is some darkening of the surfaces. This reduced materials become highly electrically conducting. Resistance of the material particularly on the surface dropped drastically almost to zero ohm as measured by a normal electrical meter. The surfaces of the reduced samples, moreover, exhibit a distinct rainbow coloration a shown in Figure 5.

It can be seen in Figure 5 that the electrical resistivity of the sintered mixed oxide ceramic, which has been heated previously up to 750^{o}C in air for several hours, increases up to around 350^{o}C; thereafter, the resistivity increases very slowly up to 700^{o}C. The resistivity is of the order of 1.0 to 3.0 ohm.m. This increase in the resistivity of the sample is attributed slight oxidation of the metallic phase(s) rather than the increase due to the temperature coefficient of resistivity of the metallic phase like copper and iron, as the resistivity of copper or iron or its alloys is of the order of 10^{-8} Ohm.m, and the temperature coefficient of resistivity α of copper and iron is of the order of 10^{-4} K^{-1}, thus the resistivity using the relation $\rho_T = \rho_o(1 + \alpha\Delta T + \beta\Delta T^2 \cdots)$ even at 700C (973K) is still of the order of 10^{-7} ohm.m.

The fact that the resistivity remains relatively constant and of the order of a few ohm.m between 350 - 700C in air further implies that the materials have potential for use as interconnect materials in solid oxide fuel cells.

It is evident that the materials retain low resistivity when evaluated in oxidizing environment. This indicates that the materials can be used as interconnect on the cathode side where the oxidant is introduced, and also in reducing environment where the fuel such as hydrogen, or carbon based fuel is introduced.

The evidence presented in Figure 3 shows clearly that the materials behaves like a semiconductor. Such type of semiconductors, basically belong to a family of high temperature semiconductors.

In addition, it is shown that the materials, after exposed to an oxidizing environment, still retain sufficiently low electrical resistivity of the order of one or two ohm.m up to 700℃ in air. This further demonstrates that the material can be used as interconnect materials for devices such as solid oxide fuel cells operating up to 700°C in air, inert and or reducing environment. The materials in particulate form can be used in the form of a paste as a low resistance contact materials for devices operating at elevated temperature up to 750°C in oxidising, inert or reducing atmospheres.

The materials can be used as high temperature semiconductor sensors. Such type of devices are useful to monitor the performance of gas turbines, high intensity discharge lamps, thermoelectric generators (TEG), Magneto-Hydrodynamic Generators (MHD) and so on up to 750C and possibly much higher temperature because the materials with the addition of chromium oxide disclosed is sintered at 1280C without incurring any distortion or melting.

The materials disclosed are, further, found to be also magnetic down to liquid nitrogen temperature (77K). This is a rather surprising effect, as the copper oxide content is very high, around 45% by weight in the mixed and sintered ceramic oxide. XRD of the mixed sintered ceramic oxide exhibits sharp diffraction peaks. Preliminary analysis shows that the crystalline phase could be ytterbium iron cuprate.

The area of interest where the magnetic properties of the materials have important implications is when the cathode and anode materials are also magnetic. This magnetic nature of the interconnect materials are then attracted to the anode and the cathode thus enhancing the electrical contact and improving the reliability and performance of the solid oxide fuel cells. Since most of the anode materials consist of ferromagnetic nickel phase, and the novel cathode materials consist of iron and cobalt oxides phases, thus with ferromagnetic or ferrimagnetic properties, the conducting and magnetic properties of the materials of the interconnect materials are moreover, found to be magnetically attracted to the anode and cathode. The enhanced contact between the electrodes and the interconnect materials further enhances the reliability of the electrical contact, and performance of the devices as encountered in solid oxide fuel cells.

It is well known in the art that the anode, cathode and electrolyte must have matching thermal expansion to minimize thermal stresses, and mechanical damage of the ceramic components. Even slight mismatch in thermal expansion can be detrimental to the performance as the intimate contact at the interface may be compromised. Under such circumstances, the use of solid oxide fuel cell materials with some additional or inherent magnetic properties that encourage intimate contact with the multilayer components, are highly desirable, and should be beneficial to the performance of the devices.

The microstructures developed in the reducing butane flame is also found to be unique in the sense that after a short exposure (2 - 5 minutes) in the reducing butane flame, the surface of the materials is reduced to a metallic state, causing the materials to be attracted to cathode and anode that are also magnetic for enhanced contacts and performance of solid oxide fuel cells. The bulk inside the sample is still in the sintered mixed oxide ceramic state. We have thus produced a composite material which is metallic on the outside and non metallic in the interior. Such type of structure can be designated as topological conductor. If the surface is superconducting, the interior is semiconducting, conducting or insulating; this

is a topological superconductor. Likewise if the surface is insulating, and the interior is electrically conducting, this is basically a topological insulator. These types of materials have useful properties and numerous applications.

It is of interest to mention that the materials without the chromium oxide melt around 1050℃. This is depicted clearly in Figure 7.

The materials as can be clearly seen in Figure 7 wet a polycrystalline alumina substrate, and flow down the alumina cylinder. The materials without the chromium oxide can therefore be used as a low temperature sealing material in the planar design of the solid oxide fuel cells.

The materials with addition of chromium oxide moreover, does not show any distortion or melting even at 1280℃ in air when place on a similar alumina substrate. These materials with the chromium oxide are also electrically conducting and as disclosed can be used as interconnect materials up to 750C in oxidizing, inert and reducing environment.

It is of interest to stress that sealing material is absolutely vital to seal the components hermetically to prevent the fuel from the anode chamber mixing with the oxidant such as air or oxygen in the cathode chamber. The mixing of the fuels and the oxidant leads to serious deterioration of the anode and high likelihood of explosion when oxygen from the air or pure oxygen combines with hydrogen. Low temperature sealing materials with thermal expansion closely matching the interconnect materials, anode and cathode are therefore highly desirable.

The disclosed invention is suitable, but not restricted to, for use in low and intermediate temperature solid oxide fuel cells ranging from 350℃ to 750℃ in oxidizing as well as in reducing environment. There are potential applications in high end designer jewelries and thus valuable materials in the leisure and fashion industries. The invention can be used as high temperature semiconductor sensors up to 750℃ in air, inert and reducing environment.