ELECTROCHEMICAL CELL

FIELD OF THE INVENTION

The present invention relates to electrochemical cells, to stacks of such electrochemical cells, and to methods of producing such electrochemical cells.

BACKGROUND OF THE INVENTION

Electrochemical cells formed of oxide layers (often known as solid oxide cells: SOC) may be used as fuel cells or electrolyser cells.

SOC fuel cells produce electricity using an electrochemical conversion process that oxidises fuel. SOC fuel cells can also, or instead, operate as regenerative fuel cells (or reverse fuel cells), often known as solid oxide electrolyser fuel cells, for example to separate hydrogen and oxygen from water, or carbon monoxide and oxygen from carbon dioxide.

A solid oxide fuel cell (SOFC) generates electrical energy through the electrochemical oxidation of a fuel gas. The device is generally ceramic-based, using an oxygen-ion conducting metal-oxide containing ceramic as its electrolyte. Ceramic oxygen ion conductors (for instance, doped zirconium oxide or doped cerium oxide) may have useful ion conductivities at temperatures in excess of 500°C (for cerium-oxide based electrolytes) or 650°C (for zirconium oxide-based ceramics), so SOFCs tend to operate at elevated temperatures.

In operation, the electrolyte of the SOFC conducts oxygen ions from a cathode to an anode located on opposite sides of the electrolyte. A fuel, for example a fuel derived from the reforming of a hydrocarbon or alcohol, contacts the anode (usually known as the “fuel electrode”) and an oxidant, such as air or an oxygen rich fluid, contacts the cathode (usually known as the “air electrode”).

Conventional ceramic-supported (e.g. anode-supported) SOFCs have low mechanical strength and are vulnerable to fracture. Hence, metal-supported SOFCs have recently been developed which have the active fuel cell component layers supported on a metal substrate. In these cells, the ceramic layers can be very thin since they only perform an electrochemical function: that is to say, the ceramic layers are not self-supporting but rather are thin

coatings/films laid down on and supported by the metal substrate. Such metal supported SOFC stacks are more robust, lower cost, have better thermal properties than ceramic-supported SOFCs and can be sealed using conventional metal welding techniques.

Applicant's earlier patent application WO-A-2015/136295 discloses metal-supported SOFCs in which the electrochemically active layer (or active fuel cell component layer) comprises anode, electrolyte and cathode layers respectively deposited (e.g. as thin coatings/films) on and supported by a metal support plate (e.g. foil). WO-A-2023/052780 discloses electrochemical cells, electrodes for electrochemical cells, methods of producing such electrochemical cells and materials for use in such electrodes.

A solid oxide electrolyser cell (SOEC) may have the same structure as an SOFC but is, in practice, an SOFC operating in reverse, or in a regenerative mode, to achieve the electrolysis of water and/or carbon dioxide.

The fuel electrode, electrolyte and air electrode of an SOC may each be formed of one or more layers to optimise operation. Effective air electrode materials allow diffusion of oxygen to the air electrode / electrolyte interface and have a similar thermal expansion coefficient to the electrolyte. The air electrode in some SOCs may be formed of an active layer close to the electrolyte which has high activity for electrochemical reduction of oxygen, and a bulk layer which may be a conductor. The nature of the various layers of an SOC may affect the operation of the cell and may improve or reduce its efficiency. The interaction between layers may also affect the operation of a cell, for example, the diffusion of a component in one layer into another may result in undesirable reaction products being formed.

There is a continuing need, therefore, to provide materials and layers that improve the operation of electrochemical cells to provide for improved efficiency of the cell.

It is an aim of the present invention to address such a need.

SUMMARY OF THE INVENTION

The present invention accordingly provides, in a first aspect, an electrochemical cell comprising :

a first electrolyte layer comprising a material having a composition $Ce_{(1-x-y)}Pr_xLn_yO_{(2-\delta)}$,

wherein Ln is selected from at least one rare earth metal,

$0.1 \leq x \leq 0.7$

$0 \leq y \leq 0.2$, and

δ is the degree of oxygen deficiency.

The advantages of such a first electrolyte layer in an electrochemical cell are that the first electrolyte layer provides improved electrochemical activity of the cell by acting as a diffusion barrier between other layers of the cell (for example, electrode layers and other electrolyte layers) and/or by reducing the resistance that may occur at the interface between the first electrolyte layer and other layers of the cell (for example an electrode layer), especially polarisation resistance.

The rare earth metal may be selected from a lanthanoid, Sc, Y and mixtures thereof.

The rare earth metal may be selected from La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Sc, Y and mixtures thereof. Preferred Ln include wherein the rare earth metal is selected from La, Sm, Gd, and Yb; preferably Gd.

Ln preferably excludes Pr.

Ln preferably excludes Ce.

The values x and y may be referred to as a metal %, determined as a percentage of the total metal species (i.e. cations) in the material. For example, $Ce_{0.75}Pr_{0.2}Ln_{0.05}O_{(2-\delta)}$, may be referred to as having a metal % (or cation%) of Pr of 20%, a metal% (cation %) of Ln as 5%, and a metal % (cation%) of Ce as 75%.

Values of x of 0.1 or higher (i.e. Pr 10 cation % or higher) surprisingly provide good properties. Values of x of 0.2 or higher (i.e. Pr 20 cation% or higher) have further improved properties, especially as regards lower resistance of the cell.

Thus, optionally x is 0.1 or higher, optionally x is 0.15 or higher, optionally x is 0.17 or higher, optionally x is 0.19 or higher, optionally x is 0.2 or higher. Values of x higher than 0.2 provide further improved properties that may include improved polarisation resistance. Thus, optionally x is 0.22 or higher, optionally x is 0.25 or higher, optionally x is 0.27 or higher, optionally x is 0.3 or higher.

Values of x of 0.7 or lower (i.e. Pr 70 cation % or higher) surprisingly provide good properties. Values of x of 0.55 or lower (i.e. Pr 55 cation% or lower) have further improved properties.

Thus, optionally x is 0.7 or lower, optionally x is 0.65 or lower, optionally x is 0.6 or lower, optionally x is 0.57 or lower, optionally x is 0.55 or lower, optionally x is 0.52 or lower, optionally x is 0.5 or lower.

Thus, optionally $0.1 \leq x \leq 0.65$, optionally $0.1 \leq x \leq 0.6$, optionally $0.1 \leq x \leq 0.55$, optionally $0.1 \leq x \leq 0.5$, optionally $0.15 \leq x \leq 0.7$, optionally $0.19 \leq x \leq 0.6$, optionally $0.19 \leq x \leq 0.55$, optionally $0.2 \leq x \leq 0.5$.

Values of y of 0.07 (i.e. Ln cation% 0.07) or lower, optionally 0.06 or lower, optionally 0.05 or lower are useful.

Thus, optionally $0 \leq y \leq 0.1$, optionally $0 \leq y \leq 0.07$, optionally $0 \leq y \leq 0.06$.

Suitably, the total cation% of Pr and Ln (i.e. x + y) is 70% or lower, optionally 55% or lower, optionally 50% or lower.

Thus, optionally $0.1 \leq (x + y) \leq 0.7$, optionally $0.1 \leq (x + y) \leq 0.55$, optionally $0.2 \leq (x + y) \leq 0.5$.

In a preferred embodiment, y is substantially 0. In such an embodiment, the first electrolyte layer therefore comprises a material having a composition $Ce_{(1-x)}Pr_xO_{(2-\delta)}$, where $0.1 \leq x \leq 0.7$

It is preferred that the cation% of Pr is the same or higher than the cation% of Ln. Thus, preferably $x \geq y$. More preferably the cation% of Pr is higher than the cation% of Ln, thus preferably $x > y$.

δ may vary depending on the environment and history of the material of the first electrolyte layer. For example, in an oxidising environment, praseodymium may be in a thermodynamic equilibrium between its +3 and +4 oxidation states, dependent upon material, the temperature and oxygen partial pressure. When Pr^{4+} is reduced to Pr^{3+} an oxygen vacancy is created. Oxygen vacancies induced by praseodymium reduction are known as extrinsic vacancies.

In the material of the first electrolyte layer, δ may be 0.25 or lower, optionally δ may be 0.2 or lower optionally δ may be ≤ 0.15.

δ may have a lower limit of 0.0001 or higher, optionally 0.001 or higher, optionally 0.005 or higher, optionally 0.01 or higher, optionally 0.05 or higher.

The addition of (e.g. trivalent) dopant cations may create intrinsic oxygen vacancies in the structure.

The first electrolyte layer may be relatively thin yet still be effective.

Thus, the first electrolyte layer may have a thickness of 1 μm or lower, optionally 750 nm or lower, optionally 650 nm or lower, optionally 500 nm or lower, optionally 450 nm or lower, optionally 400 nm or lower, optionally 350 nm or lower.

The first electrolyte layer may have a thickness of 100 nm or higher, optionally 150 nm or higher, optionally 200 nm or higher, optionally 250 nm or higher.

Thus, the first electrolyte layer may have a thickness in the range 100 nm to 1 μm, optionally 150 nm to 800 nm, optionally 200 nm to 700 nm, optionally 200 nm to 600 nm, optionally 200 nm to 500 nm, optionally 250 nm to 400 nm, optionally 250 nm to 350 nm.

The material of the first electrolyte layer may comprise a material having a cubic crystalline structure; preferably a fluorite crystalline structure. Thus, the first electrolyte layer may comprise a material having at least one phase having a fluorite structure.

The electrochemical cell preferably further comprises a second electrolyte layer. The first electrolyte layer may be directly in contact with the second electrolyte layer (i.e. a face of the first electrolyte layer may be in contact with a face of the second electrolyte layer). Alternatively, there may be a layer disposed between the first electrolyte layer and the second electrolyte layer.

The second electrolyte layer may be referred to as an interlayer.

The second electrolyte layer may comprise zirconia, optionally rare earth doped zirconia.

Thus, the second electrolyte layer may comprise zirconia doped with at least one rare earth element selected from Y, Sc or a lanthanide, optionally wherein the second electrolyte layer comprises a material selected from scandia stabilised zirconia (ScSZ), yttria stabilised zirconia (YSZ), ytterbia stabilised zirconia (YbSZ), scandia ceria co-stabilised zirconia (ScCeSZ), scandia yttria co-stabilised zirconia (ScYSZ) and mixtures thereof.

The thickness of the second electrolyte layer may be in the range 0.5 μm to 5 μm, optionally in the range 0.5 μm to 5 μm; optionally 0.5 μm to 4 μm; optionally 0.5 μm to 3 μm; or optionally 0.5 μm to 2 μm.

The second electrolyte layer, e.g. of doped zirconia, may be an electrically insulating layer of the electrolyte which advantageously provides a substantially electronically insulating layer.

The electrochemical cell may further comprise a third electrolyte layer.

The second electrolyte layer may be directly in contact with the third electrolyte layer (i.e. a face of the second electrolyte layer may be in contact with a face of the third electrolyte layer).

The third electrolyte layer may comprise doped zirconia or doped ceria.

The third electrolyte layer may comprise zirconia doped with at least one rare earth element selected from Y, Sc or a lanthanide, optionally wherein the third electrolyte layer comprises a material selected from scandia stabilised zirconia (ScSZ), yttria stabilised zirconia (YSZ), ytterbia stabilised zirconia (YbSZ), scandia ceria co-stabilised zirconia (ScCeSZ), scandia yttria co-stabilised zirconia (ScYSZ) and mixtures thereof.

Preferably, the third electrolyte layer may comprise doped ceria, optionally wherein the electrolyte comprises rare earth doped ceria.

Thus, the third electrolyte layer may comprise at least one electrolyte layer comprising a material selected from samarium-doped ceria (SDC), gadolinium-doped ceria (GDC also referred to as ceria gadolinium oxide, CGO), praseodymium doped ceria (PDC), samaria-gadolinia doped ceria (SGDC) and mixtures thereof.

The dopant concentration in the rare earth doped ceria may optionally be 20 atom % or lower.

The dopant concentration in the rare earth doped ceria may be 3 atom % or higher, optionally 5 atom % or higher, optionally 9 atom % or higher, optionally 10 atom % or higher.

Thus, the dopant concentration in the rare earth doped ceria may optionally be in the range 9 to 20 atom %, optionally 10 to 20 atom %.

The third electrolyte layer may have a thickness of 17 μm or lower. Optionally, the third electrolyte layer may have a thickness of 15 μm or lower, optionally 12 μm or lower.

The third electrolyte layer may have a thickness of 2 μm or greater. Optionally, the third electrolyte layer may have a thickness of 4 μm or greater, 5 μm or greater, 6 μm or greater or 7 μm or greater.

Thus, the third electrolyte layer may have a thickness in the range 2 μm to 17 μm, a thickness in the range 4 μm to 17 μm, a thickness in the range 5 μm to 15 μm, or a thickness in the range 6 μm to 12 μm.

The electrochemical cell may further comprise at least a first electrode layer contacting the first electrolyte layer. It is preferred that the first electrode layer is directly in contact with the first electrolyte layer (i.e. a face of the first electrolyte layer may be in contact with a face of the first electrode layer).

This is advantageous because it appears that contact between the first electrode layer and the first electrolyte layer may reduce resistance especially polarisation resistance and/or improve the overall electrochemical activity of the cell.

The first electrode layer may comprise a material that is electrically conductive, optionally the first electrode layer may comprise a material that is an electrically conductive ceramic material.

The first electrode layer may comprise doped ceria, optionally the first electrode layer may comprise ceria gadolinium oxide (CGO).

The first electrode layer may comprise a perovskite material. For example, the first electrode layer may comprise a strontium containing material, optionally selected from rare earth strontium cobaltite; rare earth strontium ferrite, rare-earth strontium cobalt ferrite, rare earth containing strontium manganite, or mixtures thereof.

An advantage of the present disclosure is that the first electrolyte layer acts as an effective diffusion barrier layer reducing or preventing the diffusion of components of e.g. the first electrode layer into other layers of the electrolyte (for example into the second electrolyte layer). For example, where Sr is present in the first electrode layer, and the second electrolyte layer comprises zirconia, the first electrolyte layer of the disclosure is effective as a diffusion barrier reducing or preventing diffusion of Sr into the zirconia layer and thereby reducing or preventing the reaction between Sr and Zr which may form an insulating layer of strontium zirconate (with consequent increase in resistance of the electrochemical cell).

The first electrode layer may comprise a Pr/Ln^{II} material of composition $Pr_{(1-q)}Ln^{II}_qO_{(2-\delta)}$,

wherein Ln^{II} is selected from at least one rare earth metal, optionally Ln^{II} is selected from La, Nd, Sm, Eu, Gd, preferably Gd or Sm, more preferably Sm,

δ is the degree of oxygen deficiency, and

$0.01 \leq q \leq 0.4$.

Such a Pr/Ln^{II} material has excellent activity and other properties and does not need to contain alkaline earth metal oxides (e.g. strontium oxide). Alkaline earth metal oxides (e.g. Sr) may be problematic in electrochemical cells because they may react, in particular, with zirconia-based electrolytes.

In the Pr/Ln^{II} material, q may be selected to achieve a balance between oxygen vacancy concentration and ion-mobility e.g. 0.02 to 0.25. Advantageously, q may be in the range $0.02 \leq x \leq 0.3$; $0.03 \leq x \leq 0.3$; $0.04 \leq x \leq 0.3$; $0.05 \leq x \leq 0.3$; $0.05 \leq x \leq 0.27$; $0.05 \leq x \leq 0.25$; $0.05 \leq x \leq 0.25$; or $0.05 \leq x \leq 0.3$. Suitably, q may be from 0.08 to 0.2 or 0.08 to 0.12, more suitably q may be about 0.1; about 0.15; or about 0.2.

Suitably the Pr/Ln^{II} material may be of formula $Pr_{0.9}Ln_{0.1}O_{(1.95-\delta)}$, $Pr_{0.85}Ln_{0.15}O_{(1.925-\delta)}$, $Pr_{0.8}Ln_{0.2}O_{(1.9-\delta)}$ or mixtures thereof; wherein Ln is selected from one or more of La, Nd, Sm, Eu, Gd, or Yb; preferably Sm.

Advantageously, the Pr/Ln^{II} material may have a cubic crystalline structure; preferably a fluorite crystalline structure. The first electrode material may essentially comprise or consist of a single phase having a cubic fluorite structure, or of two or more phases having a cubic fluorite structure.

The fluorite structure of the Pr/Ln^{II} material may also be advantageous because it may provide good interfacial interaction with a first electrolyte layer comprising a material with a fluorite structure.

The first layer of the electrode may consist essentially of a first electrode material (e.g. a perovskite material or a Pr/Ln^{II} material as discussed above). Optionally, the first layer may comprise a composite layer comprising the first electrode material and at least one further material. The further material may comprise, for example, doped ceria or doped zirconia or mixtures thereof. Doped ceria may comprise cerium gadolinium oxide (CGO).

Thus, the first electrode layer may comprise a mixture of e.g. a perovskite material (e.g. rare earth containing strontium cobaltite) and doped ceria (e.g. CGO).

Thus, the first electrode layer may comprise a mixture of e.g. the Pr/Ln^{II} material and doped ceria (e.g. CGO).

The first layer may comprise 20% by weight or greater of the first electrode material; optionally 25% by weight or greater of the first electrode material; optionally 30% by weight or greater of the first electrode material; optionally 35% by weight or greater of the first electrode material; optionally 40% by weight or greater of the first electrode material; optionally 45% by weight or greater of the first electrode material; optionally 50% by weight or greater of the first electrode material; optionally 55% by weight or greater of the first electrode material; optionally 60% by weight or greater of the first electrode material.

Alternatively, the first layer may comprise 80% by weight or greater of the first electrode material; optionally 85% by weight or greater of the first electrode material; optionally 90% by weight or greater of the first electrode material; optionally 95% by weight or greater of the first electrode material.

The first electrode layer may have a thickness in the range 1 μm to 7 μm, optionally 1 μm to 6 μm; 1 μm to 5 μm; 1 to 4 μm or about 3 μm.

The electrode may be a multilayer electrode system which may provide additional and/or improved properties for the electrochemical cell. For example, the electrode may be a two-layer, three-layer, four-layer or five-layer system or may have more than five layers. Generally, each layer of the electrode system may be the same or different and, if different, may be formed of different materials and may have different properties and uses in the electrode system as a whole.

Thus, the electrochemical cell may further comprise at least a second electrode layer directly or indirectly in contact with the first electrode layer.

The material of the second electrode layer may be electrically conductive, optionally the material of the second electrode layer may be an electrically conductive ceramic material.

The material of the second electrode layer may be selected from a perovskite material, for example selected from lanthanum cobaltite, lanthanum ferrite, lanthanum nickel ferrite,

$La_{0.99}Co_{0.4}Ni_{0.6}O_{(3-\delta)}$ (LCN60), praseodymium strontium cobaltite, praseodymium doped ceria, lanthanum strontium manganese, lanthanum strontium cobaltite and mixtures thereof.

The second electrode layer may be a composite layer further comprising at least one additional second electrode layer material, optionally wherein the second electrode layer material may comprise doped ceria (e.g. CGO) and/or may comprise a strontium-containing material, optionally selected from rare earth strontium cobaltite; rare earth strontium ferrite, rare-earth strontium cobalt ferrite; wherein the rare earth component may optionally be Pr, La, Gd and/or Sm.

The second electrode layer may have a thickness in the range 10 μm to 80 μm; 15 μm to 75 μm; 17 μm to 73 μm; 20 μm to 70 μm; 20 μm to 65 μm; 20 μm to 60 μm; 25 μm to 55 μm; 30 μm to 50 μm; or 35 μm to 45 μm.

The electrochemical cell may further comprise a third electrode layer comprising a third electrode layer material, optionally disposed between the first electrode layer and the second electrode layer (and optionally in contract with both the first electrode layer and the second electrode layer).

The third electrode layer material may comprise a strontium containing material, optionally selected from rare earth strontium cobaltite; rare earth strontium ferrite, rare-earth strontium cobalt ferrite.

The third electrode layer may have a thickness in the range 1 μm to 5 μm.

The first electrode layer (and the second electrode layer and third electrode layers, where present) may be a layer of an oxidant (air) electrode.

Electrochemical cells according to the disclosure may further comprise a second electrode having at least one layer, wherein the second electrode (or the at least one layer thereof) may be in contact (direct or indirect) with the third electrolyte layer.

Optionally, at least one layer of the second electrode may comprise doped ceria, optionally ceria gadolinium oxide (CGO), and optionally a source of nickel, optionally wherein the source of nickel comprises nickel oxide.

The second electrode may comprise at least one layer comprising a transition metal CGO cermet.

The second electrode may have a thickness of 3 μm or higher, optionally 5 μm or higher, optionally 10 μm or higher, optionally 15 μm or higher.

The second electrode may have a thickness of 50 μm or lower, optionally 45 μm or lower, optionally 40 μm or lower, optionally 35 μm or lower.

The second electrode may be a fuel electrode.

An electrochemical cell according to the disclosure may be an electrolytic cell, an oxygen separator, a sensor or a fuel cell. Optionally, the electrochemical cell may comprise a solid oxide electrochemical cell.

Thus, the electrochemical cell may be a fuel cell, or an electrolyser cell. The cell may be based upon a solid oxide electrolyte.

In fuel cell mode, a fuel may, in use, contact the anode (fuel electrode) and an oxidant, such as air or an oxygen-rich fluid, contact the cathode (air electrode). A solid oxide electrolyser cell (SOEC) may have the same structure as an SOFC, but is essentially the SOFC operating in reverse, or in a regenerative mode, to achieve the electrolysis of water and/or carbon dioxide by using the solid oxide electrolyte to produce hydrogen gas and/or carbon monoxide and oxygen.

The electrochemical cell may be a metal-supported solid oxide cell, where the layers of the electrochemical cell are supported by a metallic substrate/metal support plate.

The support plate may comprise a steel support plate, optionally a stainless steel support plate.

Metal substrates may be a metallic foil (i.e. solid metal) in which openings are provided. That has an advantage in that the porosity can be tailored and positioned in specific areas of the substrate. Alternatively, or in addition, a metal substrate may have inherent porosity (e.g. isotropic porosity) formed for example as tape cast by powder depositing a film that is then sintered to form a porous substrate. References herein to metal substrates or a porous steel sheet may refer to either of these.

The metal support plate may have a porous region surrounded by a non-porous region with the active layers being deposited upon the porous region so that gases may pass through the pores from one side of the metal support plate to the opposite side to access the active layers coated thereon. The porous region may comprise small apertures (holes drilled through the

metal foil substrate) extending through the support plate, overlying the anode (or cathode, depending on the orientation of the electrochemically active layers). Thus, the porous region of the support plate may comprise drilled holes through the support plate in the porous region, optionally may comprise laser drilled holes through the support plate in the porous region.

Electrochemical cells according to the first aspect may be such that the electrochemically active area may be disposed on the porous region of the support on a first surface of the support plate and may further comprise an interconnect (e.g. a metallic, particularly a stainless steel interconnect) (directly or indirectly) attached and electrically connected to a second surface of the support plate.

Electrochemical cell units may be arranged in a stack of electrochemical cell units, electrically connected in series. In such stacks electrical connection between cell units may rely on touch-contact of an interconnect of one electrochemical cell unit with an electrode of another electrochemical cell unit.

Thus, in a second aspect, the present invention provides, a stack of electrochemical cells, wherein each electrochemical cell is according to the first aspect.

The first electrolyte layer may be produced by depositing suitable precursor materials.

Thus, in a third aspect, the present invention provides a method of producing an electrochemical cell, the method comprising:

providing a substrate, optionally having deposited thereon at least one electrochemically active layer,

applying a first electrolyte layer composition comprising a source of Ce, a source of Pr and optionally a source of Ln on to the substrate,

optionally drying, and

optionally sintering the first electrolyte layer;

thereby forming a first electrolyte layer comprising a material having a composition $Ce_{(1-x-y)}Pr_xLn_yO_{(2-\delta)}$,

wherein Ln is selected from at least one rare earth metal,

$0.1 \leq x \leq 0.7$

$0 \leq y \leq 0.2$, and

δ is the degree of oxygen deficiency.

Applying the first electrolyte layer composition may be by printing, optionally roller printing, jet printing or screen-printing, or by spraying (for example atomised spraying), or by vapor deposition such as using chemical vapor deposition (CVD), or using physical vapor deposition (PVD). The first electrolyte layer may be composed of one or more sublayers (each formed by e.g. repeating the step of applying a first electrolyte layer composition and optionally drying and optionally sintering), for example 1 to 6 sublayers, optionally 1 to 4 sublayers, optionally 1 to 3 sublayers, optionally 1 to 2 sublayers.

After applying the first electrolyte layer composition, the composition may be dried and then may be sintered. Subsequent layers of the electrochemical cell may be applied after sintering. This is particularly advantageous if subsequent layers to be deposited (e.g. a first electrode layer) comprise alkali earth metals (e.g. Sr) because sintering the first electrolyte layer before applying subsequent layers may improve the diffusion barrier properties of the first electrolyte layer.

Advantageously, the substrate may have deposited thereon the second electrolyte layer which provides a good surface on which to deposit the first electrolyte layer.

In some embodiments, the method may further comprise:

applying a first electrode layer composition on to the first electrolyte layer before sintering,

optionally drying, and

co-sintering the first electrolyte layer and the first electrode layer.

The first electrode layer composition may comprise a source of Pr and a source of Ln^{II}, and in this case co-sintering the first electrolyte layer and the first electrode layer may be particularly advantageous because the resulting electrode may have significantly lower area specific resistance than conventional electrodes and, in particular, a significantly lower polarisation resistance. Furthermore, co-sintering is advantageous because it allows production with fewer steps.

Preferably, the first electrode layer composition may comprise $Pr_{(1-q)}Ln^{II}_{q}O_{(2-\delta)}$, wherein Ln^{II} is selected from at least one rare earth metal, optionally Ln^{II} is selected from La, Nd, Sm, Eu,

Gd, preferably Gd or Sm, more preferably Sm, δ is the degree of oxygen deficiency, and $0.01 \leq q \leq 0.4$.

Sintering or co-sintering may be performed at a temperature in the range 750 °C to 900 °C, preferably from 810 °C to 900 °C, preferably from 820 °C to 890 °C.

Sintering may be performed in an air atmosphere.

The first electrolyte layer, first electrode layer and/or other layers of the electrochemical cell may be pressed, optionally isostatically pressed, before and/or during sintering to improve adhesion and other properties.

In a fourth aspect, the present invention provides an electrochemical cell comprising: a first electrolyte layer comprising a material having a composition $Ce_{(1-x-y)}Pr_xLn_yO_{(2-\delta)}$,

in contact with a first electrode layer comprising a material of composition $Pr_{(1-q)}Ln^{II}_qO_{(2-\delta)}$,

wherein Ln is selected from at least one rare earth metal,

$0.1 \leq x \leq 0.7$,

$0 \leq y \leq 0.2$,

Ln^{II} is selected from at least one rare earth metal, optionally Ln^{II} is selected from La, Nd, Sm, Eu, Gd, preferably Gd or Sm, more preferably Sm,

$0.01 \leq q \leq 0.5$, and

δ is the degree of oxygen deficiency.

The fourth aspect is greatly advantageous because the first electrode layer and the first electrolyte layer being in direct contact may reduce resistance of the electrochemical cell, especially polarisation resistance and/or improve the overall electrochemical activity of the cell.

In a fifth aspect, the present invention provides an electrochemical cell comprising:

a first electrolyte layer,

a first electrode layer, the first electrode layer contacting the first electrolyte layer,

wherein the first electrolyte layer comprises a material having composition $M^{I}_{1-a}M^{II}_aO_{2-\delta}$,

wherein the first electrode layer comprises a material having composition $M^{II}_{1-b}M^{III}_{b}O_{2-\delta}$,

wherein M^{I}, M^{II} and M^{III} are selected from one or more of Ln^{III}, and,

$0.01 \leq a \leq 0.7$,

$0.01 \leq b \leq 0.5$,

δ is degree of oxygen deficiency,

wherein Ln^{III} is selected from one or more of Y, Sc, or a lanthanide.

In the fifth aspect, optionally M^{III} may be selected from La, Nd, Sm, Eu, Gd, preferably Gd or Sm, more preferably Sm,

Optionally, M^{II} may be (or comprise) Pr.

Optionally, M^{I} may be (or comprise) Ce.

The value of a may be as discussed herein for x. The value of b may be as discussed herein for q.

The fifth aspect is greatly advantageous because the first electrode layer and the first electrolyte layer being in direct contact may reduce resistance of the electrochemical cell, especially polarisation resistance and/or improve the overall electrochemical activity of the cell.

Definitions

In this specification, the terms “rare earth metal” or “rare earth element” refer to metals selected from Y, Sc, and lanthanoid.

“Lanthanoid”, “lanthanide” and “Ln” are used interchangeably and mean the metallic chemical elements with atomic numbers 57–71.

The term "dopant" as used herein is not intended to be restricted to a maximum percentage of elements, ions or compounds added to chemical structures. Similarly, the term "doping" is intended to mean the addition of a certain amount of elements, ions or compounds to a material. It is not limited to a maximum quantity of material, after which, further addition of material no longer constitutes doping.

The term "perovskite structure" as used herein refers to a network of chemically bonded crystal structures which have a generally perovskite (ABX_3) structure.

The term “fluorite structure” refers to crystal structure which has a generally fluorite (MX_2) structure.

Use of the term “perovskite structure” or the term “fluorite structure” is not intended to mean that materials as disclosed herein have a single, uniform crystal structure throughout the entire structure.

The term "solid oxide cell" (SOC) is intended to encompass both solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs).

Metal oxides including mixed metal oxides may exhibit non-stoichiometry with the oxide being deficient in oxygen. In this specification, δ indicates the degree of oxygen deficiency of a material. δ may vary depending on the environment and history of the material. As would be understood by the skilled person, values of δ are usually small. Thus, δ may be 0.25 or lower, suitably 0.2 or lower and more suitably ≤ 0.15. δ may have a lower limit of 0.0001, optionally 0.001, optionally 0.005, optionally 0.01, optionally 0.05.

The term “source of” an element, compound or other material refers to a material comprising the element, compound or other material whether or not chemically bonded in the source. The source of the element, compound or other material may be an elemental source (e.g. Ln, Sm, Pr or O_2) or may be in the form of a compound or mixture comprising the element, compound or other material including one or more of those elements, compounds or materials.

In this specification references to electrochemical cell, SOC, SOFC and SOEC may refer to tubular or planar cells. Electrochemical cell units may be tubular or planar in configuration. Planar electrochemical cell units may be arranged overlying one another in a stack arrangement, for example 100-500 cell units in a stack, with the individual cell units arranged electrically in series.

Electrochemical cells may be fuel cells, reversible fuel cells or electrolyser cells. Generally, these cells may have the same structure and reference to electrochemical cells may refer (unless the context suggests otherwise) to any of these types of cell.

"Oxidant electrode" or "air electrode" and "fuel electrode" are used herein and may be used interchangeably to refer to cathodes and anodes respectively of SOFCs or anodes and cathodes respectively of SOECs.

The cells described herein include metal supported cells where the layers of the cell are supported by a metallic substrate, but the invention also encompasses anode supported, electrolyte supported or cathode supported cells where the respective layer provides the structural support for all the other layers coated thereon.

Electrochemical cells as encompassed by the invention may comprise a) two planar components welded together with fluid volume in between (e.g. substrate with electrochemical layers and interconnector (separate plate)); b) three planar components welded together with fluid volume in between (e.g. substrate with electrochemical layers and interconnector (separate plate) and spacer providing fluid volume).

The various features of aspects of the disclosure as described herein may be used in combination with any other feature in the same or other aspect of the disclosure, if needed with appropriate modification, as would be understood by the person skilled in the art.

Furthermore, although all aspects of the invention or disclosure preferably "comprise" the features described in relation to that aspect, it is specifically envisaged that they may "consist" or "consist essentially" of those features outlined in the claims.

It will be understood that "attached" and "on" refer to direct or indirect attachment and positioning, respectively.

It will be understood that each layer may be comprised of multiple sub-layers (and those sub-layers may have varying compositions).

It will be understood that layers of the electrochemical cell may be composite layer comprise a mixture of two or more materials.

The invention will now be described with reference to accompanying figures and examples.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows a schematic cross section of an electrochemical cell in accordance with the disclosure.

Figure 2 is a graph showing open circuit voltage at 570°C for electrochemical cells according to the disclosure with a first electrode layer of a mixture of $Pr_{0.9}Sm_{0.1}O_{(2-\delta)}$ (abbreviated as PSmO10) and CGO (abbreviated as PSmO10/CGO);

Figure 3 shows normalised area specific resistance (ASR) as a function of Pr dopant level in the first electrolyte layer (TPDC) (610°C, SOFC mode) for an electrochemical cell having a first electrode layer of PSmO10/CGO;

Figure 4 shows normalised ASRs (ohmic resistance) as a function of Pr dopant level in the first electrolyte layer (TPDC) (510°C thermoneutral SOEC mode) for an electrochemical cell having a first electrode layer of PSmO10/CGO;

Figure 5 shows normalised SecASRp (polarisation resistance) as a function of Pr dopant level in the TPDC (510°C thermoneutral SOEC mode) for an electrochemical cell having a first electrode layer of PSmO10/CGO;

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 shows, schematically and not to scale (for reasons of clarity), a cross section of an electrochemical cell 2.

A substrate, formed by a ferritic stainless steel metal support 4, is plate-like with a peripheral, non-porous region 6 and a central, porous region 8 where holes have been drilled (e.g. laser-drilled) through the metal support 4. A barrier layer (not shown) to reduce corrosion may be located on the surface of the metal support 4 (on one or both sides thereof).

A fuel electrode 10 is located on the porous region 8 of the metal support 4. The fuel electrode 10 may be formed of e.g. Ni:CGO (Ni: cerium gadolinium oxide).

A third electrolyte layer 12 of rare earth doped ceria (RE=Y, Sc or any Ln) of thickness 2 μm or greater (optionally 6 μm to 12 μm) is located on the fuel electrode 10. The third electrolyte layer 12 may surround the fuel electrode 10 to reduce or prevent gas leaking from the fuel side 26 to the air side 24 or vice versa. The third electrolyte layer 12 may further overlap at least part of the non-porous region 6 of the substrate/support 4.

A second electrolyte layer 14 of rare earth (RE) stabilised zirconia (RE = Y, Sc or any Ln, e.g. Yb) of thickness 0.5 μm or greater (e.g. 1 μm to 4 μm) is located on the third electrolyte layer 14.

A first electrolyte layer 16 of cerium-praseodymia oxide (with optional dopant of a rare earth metal) of thickness 100 nm to 1 μm is located on the second electrolyte layer 14, and is in direct contact with the second electrolyte layer 14.

The electrochemical cell 2 has an air electrode 18, 22 comprising a first air electrode layer 18 of, for example, rare earth strontium cobaltite / ceria-gadolinia oxide (e.g. RE SC/CGO) or rare earth doped praseodymia (optionally with CGO) located on the first electrolyte layer 16 and directly in contact with the first electrolyte layer 16. The air electrode has a second air electrode layer 22 (that may act as a bulk cathode layer in SOFC mode) of an electrically conductive perovskite material.

Examples

In the following examples, electrochemical cells were produced.

Each cell comprises porous ferritic stainless steel support with a fuel electrode layer, a third electrolyte layer of CGO and a rare earth doped zirconia layer as an electron blocking layer (second electrolyte layer). The first electrolyte layer of $Ce_{(1-x-y)}Pr_xGd_yO_{(2-\delta)}$, (also referred to as TPDC, with varying Pr content and Gd either 5 cation% or not present) was applied by solution methods (e.g. inkjet printing).

Subsequent processing and sintering depended on the nature of the first electrode layer.

Where the first electrode layer comprised Sr (e.g. rare earth doped strontium cobaltite / CGO) the first electrolyte layer was dried and sintered at a temperature from 880 to 890 °C in air to form the first electrolyte layer followed by screen printing of the rare earth doped strontium cobaltite / CGO first electrode layer and subsequent electrode layers and then sintered in air at 820 °C. Attempting to combine the two thermal processes may result in strontium from the rare earth doped strontium cobaltite diffusing into the first electrolyte layer (and possibly the second electrolyte layer of doped zirconia) layer leading to poor cell performance.

Where the first electrode layer comprised PSmO10 or PSmO10/CGO, the first electrolyte layer was not sintered before screen printing of the PSmO10/CGO first electrode layer and was co-sintered at 870 to 890 °C in air resulting in improved performance.

In the electrochemical cells of the disclosure, the first (top) layer of the electrolyte (interface between the electrolyte and the air electrode) comprises a thin (<300nm) layer of praseodymia-doped ceria (optionally ceria with 20 cation% praseodymium and 5 cation% gadolinium) which provides the surprising advantages of providing a diffusion barrier between the a rare earth doped strontium cobaltite / CGO air electrode layer and the zirconia-based electron blocking layer (second electrolyte layer) to reduce or prevent reaction between strontium and zirconium to form an insulating layer of strontium zirconate; and improving the electrochemical activity of the air electrode: air electrodes interfacing with ceria have lower polarisation resistance than air electrodes interfacing with zirconia.

In the examples, the effect of varying the dopant level in the first electrolyte layer (e.g. between 10 cation% Pr and 50 cation% Pr has been studied and compared to a ceria with 20% Pr and 5% Gd).

Electrochemical cells were made and placed in 15 cell stacks and tested in both SOFC and SOEC modes.

For SOFC performance three power points were run, all fuelled by simulated steam reformed natural gas at a composition equivalent to a thermodynamic equilibrium of 545°C with a steam:carbon ratio of 2.5. All points were run at 610°C stack air outlet temperature.

90mA/cm^2 60% fuel utilisation,

133mA/cm^2 75% fuel utilisation, and

185mA/cm^2 75% fuel utilisation.

The SOEC performance test involved running the stack in electrolysis mode at three temperatures:

510°C,

530°C, and

550°C.

At each temperatures an IV curve was run until the stack on average reaches the thermoneutral voltage (about 1.28 V/ cell), at which point there is no net thermal input or output from the electrochemical reaction. The cells are fed with a mixture of 95% steam and 5% hydrogen, and run to 75% oxygen utilisation. AC impedance spectroscopy was run at each point to allow ohmic resistance to be separated from polarisation resistance.

A selection of the results are shown in Figures 2 to 5.

Figure 2 shows that open circuit voltage (SOFC mode) at 570°C for electrochemical cells with PSmO10/CGO and PSC/CGO air electrodes co-fired with the TPDC provide high open circuit voltages of > 1.2V.

Figure 3 (area specific resistance as a function of Pr dopant level in the TPDC; 610°C, SOFC mode) shows a reduction in ASR with Pr content for PSmO10 electrodes.

Figure 4 (ASRs, ohmic resistance as a function of Pr dopant level in the TPDC; 510°C thermoneutral SOEC mode) shows a correlation between Pr-content in the TPDC and ASRs for the PSmO10/CGO cells.

Figure 5 shows strong correlation between Pr-content in the TPDC and ASRp for the PSmO10/CGO cells. PSmO10/CGO air electrodes have lower polarisation resistance overall.

For the PSC/CGO air electrode there is a performance benefit in increasing the Pr content beyond 20%, and for PSmO10/CGO air electrodes, performance increased with praseodymium content up to 50%, with >30% showing significantly lower polarisation resistance than <30%, particularly at low temperatures.

In addition there is a clear trend with PSmO10/CGO air electrodes that increasing the Pr content in the TPDC between 10 and 50% results in lower ASR, particularly polarisation resistance but also to some extent ohmic resistance at lower temperatures

Co-sintering a PSmO10/CGO active air electrode with an 40-50% Pr-doped TPDC seems to offer significant performance enhancement over conventional cells.

REFERENCE NUMERALS

2 electrochemical cell

4 metal support

6 non-porous region of metal support

8 porous region of metal support

10 fuel electrode

12 third electrolyte layer

14 second electrolyte layer

16 first electrolyte layer

18 first air electrode layer

22 second air electrode layer

24 air side

26 fuel side.

All publications mentioned in the above specification are herein incorporated by reference. Although illustrative embodiments of the invention have been disclosed in detail herein, with reference to the accompanying drawings, it is understood that the invention is not limited to the precise embodiment and that various changes and modifications can be performed therein by one skilled in the art without departing from the scope of the invention as defined by the appended claims and their equivalents.

CLAIMS

1. An electrochemical cell comprising:

a first electrolyte layer comprising a material having a composition $Ce_{(1-x-y)}Pr_xLn_yO_{(2-\delta)}$,

wherein Ln is selected from at least one rare earth metal,

$0.1 \leq x \leq 0.7$

$0 \leq y \leq 0.2$, and

δ is the degree of oxygen deficiency.

2. An electrochemical cell as claimed in claim 1, wherein the rare earth metal is selected from a lanthanoid, Sc, Y and mixtures thereof.

3. An electrochemical cell as claimed in claim 2, wherein the rare earth metal is selected from La, Sm, Gd, and Yb; preferably Gd.

4. An electrochemical cell as claimed in any one of the preceding claims, wherein $0.1 \leq x \leq 0.65$, optionally wherein $0.1 \leq x \leq 0.6$, optionally $0.1 \leq x \leq 0.55$, optionally $0.1 \leq x \leq 0.5$, optionally $0.15 \leq x \leq 0.7$, optionally $0.19 \leq x \leq 0.6$, optionally $0.19 \leq x \leq 0.55$, optionally $0.2 \leq x \leq 0.5$.

5. An electrochemical cell as claimed in any one of the preceding claims, wherein $x \geq y$, preferably wherein $x > y$.

6. An electrochemical cell as claimed in any one of the preceding claims, wherein y is substantially 0.

7. An electrochemical cell as claimed in any one of the preceding claims, wherein the first electrolyte layer has a thickness of 1 μm or lower, optionally 750 nm or lower, optionally 650 nm or lower, optionally 500 nm or lower, optionally 450 nm or lower, optionally 400 nm or lower, optionally 350 nm or lower.

8. An electrochemical cell as claimed in any one of the preceding claims, wherein the first electrolyte layer has a thickness of 100 nm or higher, optionally 150 nm or higher, optionally 200 nm or higher, optionally 250 nm or higher.

9. An electrochemical cell as claimed in any one of the preceding claims, wherein the first electrolyte layer has a thickness in the range 100 nm to 1 μm, optionally 150 nm to 800 nm, optionally 200 nm to 700 nm, optionally 200 nm to 600 nm, optionally 200 nm to 500 nm, optionally 250 nm to 400 nm, optionally 250 nm to 350 nm.

10. An electrochemical cell as claimed in any one of the preceding claims, further comprising a second electrolyte layer.

11. An electrochemical cell as claimed in any one of the preceding claims, wherein the second electrolyte layer comprises zirconia, optionally rare earth doped zirconia, optionally wherein the second electrolyte layer comprises zirconia doped with at least one rare earth element selected from Y, Sc or a lanthanide (Ln), optionally wherein the second electrolyte layer comprises a material selected from scandia stabilised zirconia (ScSZ), yttria stabilised zirconia (YSZ), ytterbia stabilised zirconia (YbSZ), scandia ceria co-stabilised zirconia (ScCeSZ), scandia yttria co-stabilised zirconia (ScYSZ) and mixtures thereof.

12. An electrochemical cell as claimed in any one of the preceding claims, further comprising a third electrolyte layer.

13. An electrochemical cell as claimed in any one of the preceding claims, wherein the third electrolyte layer comprises doped ceria, optionally wherein the electrolyte comprises

rare earth doped ceria, optionally wherein the third electrolyte layer comprises at least one electrolyte layer comprising a material selected from samarium-doped ceria (SDC), gadolinium-doped ceria (GDC), praseodymium doped ceria (PDC), samaria-gadolinia doped ceria (SGDC) and mixtures thereof.

14. An electrochemical cell as claimed in any one of the preceding claims, further comprising at least a first electrode layer contacting the first electrolyte layer.

15. An electrochemical cell as claimed in any one of the preceding claims, wherein the first electrode layer comprises a material of composition $Pr_{(1-q)}Ln^{II}_qO_{(2-\delta)}$,

wherein Ln^{II} is selected from at least one rare earth metal, optionally Ln^{II} is selected from La, Nd, Sm, Eu, Gd, preferably Gd or Sm, more preferably Sm,

δ is the degree of oxygen deficiency, and

$0.01 \leq q \leq 0.4$.

16. An electrochemical cell as claimed in either claim 14 or claim 15, wherein the first electrode layer comprises doped ceria, optionally wherein the first electrode layer comprises ceria gadolinium oxide (CGO).

17. An electrochemical cell as claimed in any one of the preceding claims, further comprising at least a second electrode layer directly or indirectly in contact with the first electrode layer, optionally wherein the material of the second electrode layer is selected from lanthanum cobaltite, lanthanum ferrite, lanthanum nickel ferrite, $La_{0.99}Co_{0.4}Ni_{0.6}O_{(3-\delta)}$ (LCN60), praseodymium strontium cobaltite, praseodymium doped ceria, lanthanum strontium manganese, lanthanum strontium cobaltite and mixtures thereof.

18. An electrochemical cell as claimed in any one of claims 14 to 17, wherein the first electrode layer, and optionally the second electrode layer, is a layer of an oxidant electrode.

19. An electrochemical cell as claimed in any one of the preceding claims, further comprising a second electrode having at least one layer, wherein the second electrode is in contact direct or indirect with the third electrolyte layer.

20. A stack of electrochemical cells, wherein each electrochemical cell is as claimed in any one of the preceding claims.

21. A method of producing an electrochemical cell, the method comprising

providing a substrate, optionally having deposited thereon at least one electrochemically active layer,

applying a first electrolyte layer composition comprising a source of Ce, a source of Pr and a source of Ln on to the substrate,

optionally drying, and

optionally sintering the first electrolyte layer;

thereby forming a first electrolyte layer comprising a material having a composition $Ce_{(1-x-y)}Pr_xLn_yO_{(2-\delta)}$,

wherein Ln is selected from at least one rare earth metal,

$0.1 \leq x \leq 0.7$

$0 \leq y \leq 0.2$, and

δ is the degree of oxygen deficiency.

22. A method as claimed in claim 21, wherein the method further comprises

applying a first electrode layer to the first electrolyte layer before optional sintering,

optionally drying, and

co-sintering the first electrolyte layer and the first electrode layer.

23. An electrochemical cell comprising

a first electrolyte layer,

a first electrode layer, the first electrode layer contacting the first electrolyte layer,

wherein the first electrolyte layer comprises a material having composition $M^{I}_{1-a}M^{II}_{a}O_{2-\delta}$,

wherein the first electrode layer comprises a material having composition $M^{II}_{1-b}M^{III}_{b}O_{2-\delta}$,

wherein M^{I}, M^{II} and M^{III} are selected from one or more of Ln^{III}, and,

$0.01 \leq a \leq 0.7$,

$0.01 \leq b \leq 0.5$,

δ is degree of oxygen deficiency,

wherein Ln^{III} is selected from one or more of Y, Sc, or a lanthanide.

24. An electrochemical cell as claimed in claim 23, wherein M^{II} comprises Pr.

25. An electrochemical cell as claimed in either claim 23 or claim 24, wherein M^{I} comprises Ce.