

ELECTRODE AND ELECTROCHEMICAL CELL

FIELD OF THE INVENTION

The present invention relates to electrodes for electrochemical cells, to electrochemical cells
5 comprising such electrodes, to methods of producing such electrochemical cells and to
materials for use in such electrodes.

BACKGROUND OF THE INVENTION

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

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

A solid oxide fuel cell (SOFC) generates electrical energy through the electrochemical
oxidation of a fuel gas (usually hydrogen-based) and the device is generally ceramic-based,
using an oxygen-ion conducting metal-oxide containing ceramic as its electrolyte. Many
ceramic oxygen ion conductors (for instance, doped zirconium oxide or doped cerium oxide)
20 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 the opposite side of the electrolyte. A fuel, for example, a fuel derived from the
25 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
30 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). The metal support plate has 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 comprises 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).

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. Practical air electrode materials often have the perovskite structure ABX_3 , where A and B are different metal ions (there can be more than one A and B metal ion), X may be O. The air electrode in some SOFCs 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 metallic conductor. There are a number of known cathode materials.

Cruz Pacheco *et al.*, (*J. Phys: Conference Series*, vol. **687**, no. 1, 2016) disclose synthesis of praseodymium doped cerium oxides by the polymerization combustion method for application as anodic components in SOFC devices.

Doped praseodymium oxides have been investigated for reasons unrelated to SOC. For example, Zoellner *et al.* (*J. Crystal Growth*, vol. 355, no. 1, 2012, p. 159-165) disclose the stoichiometry-structure correlation of epitaxial cerium doped praseodymium oxide films on

- Si (111). Knauth *et al.* (*J. European Ceramic Society*, vol. 19, no. 6-7, 1999, p. 831-836) disclose non-stoichiometry and relaxation kinetics of nanocrystalline mixed praseodymium-cerium oxide. Popescu Ione *et al.* (*Applied Catalysis A: General*, vol. 578, 2019, p. 30-39) disclose studies on the catalytic oxidation performances of Ce-Pr mixed oxides. Simona Somacescu *et al.* (*J. Nanoparticle Research*; vol. 14, no. 6, 2012, p. 1-17) disclose CePrO structure, morphology, surface chemistry, and catalytic performance. Kang *et al.* (*J. Alloys and Compounds*, vol. 207-208, 1994, p. 420-423) disclose structures and structural defects in colloidal particles altered in situ in HREM.
- Tuller *et al.*, (*Energy Environ. Sci.*, 2022, **15**, 4038), describe reactivation of chromia poisoned oxygen exchange kinetics in the cerium based solid oxide $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ by serial infiltration of lithium oxide.
- US-B-6,117,582 describes a cathode composition for a solid oxide fuel cell having a cathode made from a transition metal perovskite, such as PrCoO_3 , or praseodymium manganite. US-A-2017/149067 discloses fuel cells and cathodes that may comprise nickelate compounds (e.g. Pr_2NiO_4). Nicollet, C, *et al.*, *International Journal of Hydrogen Energy*, September 2016, Vol. 41, Issue 34, pages 15538-15544, describes Pr_6O_{11} as an electrocatalyst for the oxygen reduction reaction and its use as a cathode in a SOFC. CN-A-106 057 641 discloses La, Nd and Gd doped Pr semiconductor oxides. Wang *et al* 2017 232nd ECS Meet. Abstr. (MA2017-02/39/1730) discloses $\text{Pr}_{1-x}\text{Nd}_x\text{O}_{2-\delta}$ combined with $(\text{Pr,Nd})_2\text{NiO}_4$ (PNNO) to improve the activity and phase stability of PNNO used as the cathode for solid oxide fuel cells. Biswas, R. *et al.* (1997) *Journal of Materials Science Letters*. 16. 1089-1091 discloses the preparation, structure and electrical conductivity of $\text{Pr}_{1-x}\text{La}_x\text{O}_{2-\delta}$ ($x = 0.05, 0.1, 0.2$). Zhu, *et al.* *Advanced Materials Research*, vol. 1065–1069, (2014), pp. 1921–1925 discloses the preparation and properties of $\text{Ce}_{0.8}\text{Pr}_{0.2-x}\text{Nd}_x\text{O}_{2-\delta}$ ($x=0.02, 0.05, 0.1$). WO-A-2006/106334 A1 describes a solid oxide fuel cell (SOFC) wherein the cathode material includes a doped material, having a perovskite structure, which may include praseodymium. This structure has the conventional notation ABX_3 , wherein cerium is substituted onto the “B” site.

There is still a need, however, to provide electrode materials that have suitable properties for use in electrochemical cells.

- 30 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 electrode for an electrochemical cell, the electrode comprising at least a first layer comprising a first electrode composition, the first electrode composition comprising $\text{Pr}_{(1-x)}\text{Ln}_x\text{O}_{(2-0.5x-\delta)}$ and a source of
 5 lithium,

wherein Ln is selected from at least one rare earth metal selected from La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y and mixtures thereof,

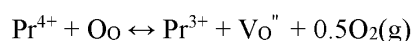
δ is the degree of oxygen deficiency, and

$$0.01 \leq x \leq 0.4.$$

10 A first electrode composition comprising Li-containing $\text{Pr}_{(1-x)}\text{Ln}_x\text{O}_{(2-0.5x-\delta)}$ is greatly advantageous because the applicant has surprisingly discovered that it increases mean cell potential especially at lower temperatures and may act as a sintering aid. Li-containing $\text{Pr}_{(1-x)}\text{Ln}_x\text{O}_{(2-0.5x-\delta)}$ may also alleviate the effect of chromium poisoning during use of a SOC, and it may also (without wishing to be bound) increase the surface reaction rate at the air
 15 electrode/electrolyte interface.

The first electrode material may be a mixed material. There may, however, be a solid solution (e.g. of Li in RE-doped praseodymia) or there may be lithium oxide (or other lithium compounds e.g. lithium carbonate) particles or nanoparticles present in the composition under some conditions (e.g. during or after sintering or in use). Thus, the first electrode material
 20 having the overall composition may be of one or more phases or a mixed material and different parts of the electrode may have different local compositions or mixed materials or phases.

δ may vary depending on the environment and history of the first electrode material. In an oxidising environment in many praseodymium-containing oxides, praseodymium is in a
 25 thermodynamic equilibrium between its +3 and +4 oxidation states, dependent upon 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. Using Kröger-Vink notation, the equilibrium may be expressed as:



30 where V_O'' is an oxygen vacancy.

In the first electrode material, 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.

- 5 The addition of (e.g. trivalent) dopant cations to praseodymium oxide creates intrinsic oxygen vacancies in the structure. In the first electrode material, suitably the rare earth metal may act as a dopant.

Suitably, the upper limit of lithium in the composition may be 7 cation %, optionally 6 cation %, optionally 5 cation %.

- 10 Suitably, the lower limit of lithium in the composition may be 0.001 cation %, optionally 0.01 cation %, optionally 0.1 cation %, optionally 1 cation %.

% cation indicates the atomic percentage (equivalent to molar percentage) based on cations in the first electrode composition (e.g. the cations Pr, Li, Ln).

- Lithium may be present in the first electrode composition in an amount of 0.001 to 5 cation
15 % . Optionally, lithium may be present in the first electrode composition in an amount of 0.01 to 5 cation %.

- Suitably, the source of lithium may be present in the first electrode composition in an amount of 0.1 to 5 cation %. More suitably, the source of lithium may be present in the first electrode composition in an amount of 0.2 to 5 cation %, 0.3 to 5 cation %, 0.5 to 5 cation %, 0.5 to 4
20 cation %, 0.5 to 3 cation %.

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

- Suitably, the rare earth metal may be selected from La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y and mixtures thereof. More suitably, the rare earth metal may be selected from La,
25 Nd, Sm, Eu, Gd, and Yb; optional selected from La, Sm, Gd, and Yb; preferably Nd, Sm, Eu, Gd, more preferably Gd or Sm, most preferably Sm.

As used in this specification, Ln indicates a dopant and thus Ln excludes Pr.

The oxides of praseodymium represent a system of phases whose composition is somewhat variable. Single phase PrO_2 generally forms in pure oxygen and at elevated pressure ($>20,000$

kPa). Among the different oxides, Pr_6O_{11} is particularly stable. At ambient temperatures and pressure, Pr_6O_{11} adopts a cubic fluorite structure with the praseodymium ions in Pr_6O_{11} being in a mixed valency state of Pr(III) and Pr(IV) with extrinsic oxygen vacancies, facilitating oxygen ion conductivity and are thought (without wishing to be bound) to provide catalytic activity.

Advantageously, the presence of a rare earth metal dopant in the first electrode material may result in the formation of additional, intrinsic, oxygen vacancies and may stabilise the cubic fluorite structure of the material.

In the first electrode material, x may be selected to achieve a balance between oxygen vacancy concentration and ion-mobility e.g. 0.02 to 0.25. Advantageously, x 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, x may be from 0.08 to 0.2 or 0.08 to 0.12, more suitably x may be about 0.1; about 0.15; or about 0.2.

Suitably, $0.02 \leq x \leq 0.25$.

Thus, suitably the first electrode material may comprise $\text{Pr}_{0.9}\text{Ln}_{0.1}\text{O}_{(1.95-\delta)}$, $\text{Pr}_{0.85}\text{Ln}_{0.15}\text{O}_{(1.925-\delta)}$, $\text{Pr}_{0.8}\text{Ln}_{0.2}\text{O}_{(1.9-\delta)}$ or mixtures thereof; and a source of lithium.

The first layer of the electrode may consist essentially of the first electrode material.

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). Doped zirconia may be a solid solution which may conform to the formula $\text{Zr}_{(1-x)}\text{Y}_x\text{O}_{(2-0.5x\delta)}$ where $0 < x \leq 0.2$.

Thus, 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.

The first 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 source of lithium may comprise any suitable lithium compound, for example, lithium oxide, lithium hydroxide, a lithium salt (e.g. lithium nitrate, lithium carbonate), a lithium salt
5 of an organic acid (e.g. lithium citrate, lithium acetate, or lithium oxalate) and/or lithium as a dopant.

The electrode may be a multilayer electrode system which provides 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.

10 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 electrode may comprise at least a second layer comprising a second electrode material. Optionally, the second electrode material may be electrically conductive, optionally
15 may be an electrically conductive ceramic material.

The second layer may have a thickness in the ranges 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 .

In a second aspect, the present invention accordingly provides an electrode for an
20 electrochemical cell, the electrode comprising at least a first layer comprising a first electrode material of composition comprising $\text{Pr}_{(1-x)}\text{Ln}_x\text{O}_{(2-0.5x-\delta)}$ and a source of lithium, and at least a second layer comprising a second electrode material; wherein Ln is selected from at least one rare earth metal selected from La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y and mixtures thereof, δ is the degree of oxygen deficiency, and $0.01 \leq x \leq 0.4$.

25 As an example, the first and second layers of the electrode system may comprise respectively the first layer as discussed above for use as an air electrode active layer (also known in SOFCs as a cathode active layer, CAL), and a second layer as an air electrode bulk layer (also known in SOFCs as a cathode bulk layer CBL). The air electrode bulk layer may have greater electrical (i.e. electron) conductivity than the first layer and may thereby act as a
30 current collector.

The first layer may be situated next to the electrolyte (which itself may be an electrolyte system comprised of multiple layers) with either an intermediate layer (e.g. a further layer of the electrode) between the first layer of the electrode and the electrolyte or wherein the first layer is directly in contact with (i.e. is immediately adjacent to) a layer of the electrolyte.

- 5 The second layer (e.g. an air electrode bulk layer) may advantageously be formed of or comprise a second electrode material that is electrically conductive e.g. that may be a metallic conductor at the operating temperature of the electrochemical cell and may have relatively high electronic conductivity at those temperatures. The second layer material is preferably chemically and mechanically stable. The second layer, e.g. the air electrode bulk layer, will
10 usually be porous (as usually will be the first layer) to allow good interaction with oxygen on the air side of the cell. The electrocatalytic activity of the second layer (e.g. air electrode bulk layer) may be less than that of the first layer (which as discussed above may have a high electrocatalytic activity).

- The second electrode material may comprise an electronically conductive ceramic material,
15 optionally having a perovskite structure, ABX_3 .

Suitable second electrode materials include lanthanum cobaltite, lanthanum ferrite, lanthanum nickel ferrite, $La_{0.99}Co_{0.4}Ni_{0.6}O_{(3-\delta)}$ (LCN60) and mixtures thereof.

- Optionally, the second layer may be a composite layer further comprising at least one additional second electrode material. The additional electrode material may comprise a
20 strontium containing material, optionally selected from rare earth strontium cobaltite; rare earth strontium ferrite, rare-earth strontium cobalt ferrite; the rare earth component may optionally be Pr, La, Gd and/or Sm, preferably Pr.

- Optionally, a composite second electrode layer may comprise 60% by weight or greater of the second electrode material; optionally 65% by weight or greater of the second electrode
25 material; optionally 70% by weight or greater of the second electrode material; optionally 75% by weight or greater of the second electrode material.

The electrode may further comprise a third layer that may comprise a third electrode material.

- To improve adhesion between the first electrode layer and the second electrode layers, if necessary, the third layer may optionally be situated between the first layer and the second
30 layer.

Optionally, the third electrode material may comprise an oxygen ion conductor. The oxygen ion conductor may preferably comprise doped ceria, or doped zirconia or mixtures thereof. The doped ceria may preferably comprise cerium gadolinium oxide (CGO), which is a solid solution having the formula, $\text{Ce}_{(1-x)}\text{Gd}_x\text{O}_{(2-0.5x-\delta)}$ where $0 < x \leq 0.5$. The doped zirconia may be

5 a solid solution which conforms to the formula $\text{Zr}_{(1-x)}\text{Y}_x\text{O}_{(2-0.5x-\delta)}$ where $0 < x \leq 0.2$.

Additionally or alternatively, the third electrode material 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; preferably Pr.

10 Optionally, the third electrode material may comprise a mixed material of rare earth strontium cobaltite or rare earth strontium ferrite and rare-earth doped ceria (REDC). A particularly suitable third electrode material may comprise 60:40 by weight of a mixture of praseodymium strontium cobaltite (e.g. PSC 551: $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$) and CGO.

The third electrode material may promote good adhesion between the first and second

15 electrode layers and may reduce any reaction in the conditions of the cell between the second electrode material (e.g. LCN60) and the first electrode material that may lead to the formation of secondary phases, which may lead to poorer adhesion and potentially increased ohmic resistance.

Furthermore, the third electrode layer may act as a poison getter for the first electrode layer

20 as contaminants in the cell may react with the third electrode material (e.g. containing strontium cobaltite/ cobalt ferrite) before contacting the first electrode layer. This advantageously protects the first electrode material and layer from degradation. Such contaminants may include chromium, silicon, and sulphur from SO_2 in the air.

The third layer may have a thickness in the range 1 μm to 5 μm ; 1 μm to 4 μm ; 2 μm to 5

25 μm ; or 2 μm to 4 μm .

The layers of the electrode (e.g. the first electrode layer, the second electrode layer and/or the third electrode layer) may be pressed, optionally isostatically pressed, during sintering to improve adhesion and other properties.

The electrode of the first aspect or the second aspect may be an air electrode.

30

The electrode of the first aspect or the second aspect may be an air electrode in an electrochemical cell, for example in a SOC, in a SOFC or in a SOEC.

Thus, in a third aspect, the present invention accordingly provides an electrochemical cell comprising an electrode according to any one of the preceding aspects; optionally further
5 comprising one or more of an electrolyte, a second electrode and a substrate. The second electrode may be a second, fuel electrode.

The electrolyte may comprise at least one electrolyte layer comprising doped ceria, optionally selected from samarium-doped ceria (SDC), gadolinium-doped ceria (GDC), praseodymium doped ceria (PDC), samaria- gadolinia doped ceria (SGDC) and mixtures thereof.

10 The electrolyte may comprise at least one electrolyte layer comprising zirconia, optionally 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 electrochemical cell may further comprise a substrate; optionally a metallic substrate,
15 preferably a steel substrate. The substrate may be porous.

Metal substrates may be a metallic foil (i.e. solid metal) in which openings are provided. That has an advantage 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
20 sintered to form a porous substrate. References herein to metal substrates or a porous steel sheet may refer to either of these.

The electrochemical cell may be an electrolyser cell, an oxygen separator, a sensor or a fuel cell, preferably a solid oxide electrochemical cell (which may be a fuel cell, SOFC, or an electrolyser cell, SOEC).

25 In fuel cell mode, a fuel contacts the anode (fuel electrode) and an oxidant, such as air or an oxygen-rich fluid, contacts the cathode (air electrode), so in fuel cell mode operation, the air electrode will be the cathode. 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
30 electrolyte to produce hydrogen gas and/or carbon monoxide and oxygen.

The electrode made be printed or otherwise applied to the substrate having layers deposited thereon.

- In a fourth aspect, the present invention accordingly provides a method of producing an electrode for an electrochemical cell, the method comprising: providing a substrate,
- 5 optionally having deposited thereon layers comprising a fuel electrode and an electrolyte, applying at least a first layer comprising a first electrode composition, the first electrode composition comprising $\text{Pr}_{(1-x)}\text{Ln}_x\text{O}_{(2-0.5x-\delta)}$ and a source of lithium, optionally drying at least said first layer, and optionally sintering the at least said first layer; thereby forming an electrode; wherein Ln is selected from at least one rare earth metal selected from La, Nd, Sm,
- 10 Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y and mixtures thereof, δ is the degree of oxygen deficiency, and $0.01 \leq x \leq 0.4$.

This is advantageous because the applicant has surprisingly discovered that the presence of a source of lithium results in much improved sintering which may lead to much improved mean cell voltage in an electrochemical cell e.g. SOFC.

- 15 Optionally, the method may further comprise, applying material to the substrate to form at least one electrolyte layer, applying the first electrode composition on the electrolyte layer to form an air electrode layer, optionally drying said air electrode layer, and co-sintering the electrolyte layer and the air electrode layer.

- The air electrode layer (e.g. the active air electrode layer, CAL) may be co-fired (i.e. co-sintered) with an underlying electrolyte material layer where both layers had been laid down sequentially as green layers (and optionally pressed). The at least one electrolyte layer (there may be other electrolyte layers) may be a layer comprising zirconia (e.g. an electron blocking layer). Co-sintering is greatly advantageous because it allows production with fewer steps.
- 20

- Sintering, or co-sintering, may be performed at a temperature in the range 750 °C to 900 °C, preferably from 790 °C to 900 °C. Sintering may be performed in an air atmosphere.
- 25

In the method, the first electrode composition may comprise $\text{Pr}_{(1-x)}\text{Ln}_x\text{O}_{(2-0.5x-\delta)}$ and a lithium salt, optionally lithium nitrate, lithium carbonate, lithium citrate, lithium acetate, and/or lithium oxalate, preferably lithium nitrate.

The method of making the material of the first electrode composition may comprise a step of:

- (a) mixing $\text{Pr}_{(1-x)}\text{Ln}_x\text{O}_{(2-0.5x-\delta)}$ and a source of lithium, optionally a source of lithium (e.g., a lithium compound) dissolved or dispersed in a solvent, preferably alcohol;
- (b) optionally drying; and
- (c) calcining the Li-containing $\text{Pr}_{(1-x)}\text{Ln}_x\text{O}_{(2-0.5x-\delta)}$ (e.g. at a temperature of 450 °C to 600 °C) to generate the material of the first electrode composition (e.g. by decomposing the lithium salt to generate lithium oxide).

The method of forming an electrode comprising at least a first electrode layer may comprise the steps of providing a suitable dispersion in a carrier of the first electrode layer material, applying a coating of the dispersion to a substrate; and sintering the coating to form the air electrode.

In a fifth aspect, the present invention provides a composition comprising $\text{Pr}_{(1-x)}\text{Ln}_x\text{O}_{(2-0.5x-\delta)}$ and a source of lithium, wherein Ln is selected from at least one rare earth metal selected from La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y and mixtures thereof, δ is the degree of oxygen deficiency, and $0.01 \leq x \leq 0.4$.

- 15 In a sixth aspect, the present invention provides a composition comprising $\text{Pr}_{(1-x)}\text{Sm}_x\text{O}_{(2-0.5x-\delta)}$ and a source of lithium, wherein δ is the degree of oxygen deficiency, and $0.01 \leq x \leq 0.4$.

In a seventh aspect, the present invention provides a stack of electrochemical cells according to the electrochemical cells of the third aspect.

20 Definitions

In this specification, the terms "lanthanoid", and "lanthanide" 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 single network of chemically bonded crystal structures which have a generally perovskite (ABX_3) structure. This does not

mean that this single network need possess a single, uniform crystal structure throughout the entire structure. However, where different crystal structures occur between different regions of the network, it is often the case that these regions have complementary structures permitting chemical bonds to more easily form there between.

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

The term "cation percent" or "cation percentage" (abbreviated herein to "cation %" or "% cation") refers to the percentage of cations with respect to the composition.

- 10 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 O₂) or may be in the form of a compound or mixture comprising the element (e.g. lithium nitrate), compound or other material including one or more of those elements, compounds or materials.

- 15 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 fuel cell units may be arranged overlying one another in a stack arrangement, for example 100-200 fuel cell units in a stack, with the individual fuel cell units arranged electrically in series.

- 20 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.

- 25 "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 because of potential confusion between fuel cells or electrolyser cells.

Although, in this specification, cells are described wherein the fuel electrode (e.g. an anode) is laid down first on the substrate, the invention also encompasses cells wherein the air electrode is laid down first on the substrate.

- 30 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.

The invention will now be described with reference to accompanying Figures and Examples.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 illustrates a scanning electron micrograph (SEM) cross-section of a SOFC with a cathode active layer (CAL) of a material according to the disclosure.

Figure 2 illustrates a scanning electron micrograph (SEM) cross-section of the SOFC of Figure 1 showing details of the CAL and adjacent layers.

Figure 3 illustrates mean cell potential as a function of temperature of cells with an CAL comprising a material according to the disclosure containing 2% lithium and sintered at 870 °C (under the conditions 133 mAcm⁻², 75% Uf, 545°C reformat equilibrium) normalised to standard cells in the same stack.

Figure 4 illustrates mean cell potential as a function of temperature of cells with an CAL comprising a material according to the disclosure containing 2% lithium and sintered at 870 °C, (under the conditions 225 mAcm⁻², 75% Uf, 545°C reformat equilibrium), normalised to standard cells in the same stack.

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 illustrates an SOC comprising a cathode active layer (CAL) 30 which includes Ln-doped praseodymium oxide (PLnO) containing a source of lithium (e.g. Li-containing PSmO10).

In Figure 1, the layers of the SOC are the bulk air electrode layer (CBL) 10, interfacial air electrode layer of ReSC/ CGO 20, the air electrode active layer comprising a composition according to the disclosure (e.g. source of lithium and PrLnO, e.g. 2LiPSmO10) (CAL) 30, a doped ceria barrier layer 35, a zirconia electron blocking layer 40, the electrolyte layer of CGO 50 and the fuel electrode 60. The fuel electrode 60 is supported on the metallic substrate (not shown).

The metallic substrate may be of a metal, especially steel, more especially a ferritic stainless steel substrate, usually a foil substrate.

The CAL 30 comprises a material according to the disclosure. The other layers are of a type whose composition is known to the skilled person, as are methods of making and applying. Reference may, for example, be made to WO 2009/090419 A2, which discusses methods for laying down, as well as exemplary compositions of, layers of these types, together with the laying down of such layers upon a metal substrate, especially upon a stainless steel substrate. The layers (including air electrode layers) may show good adhesion and/or may be isopressed to further improve adhesion.

Figure 2 illustrates a scanning electron micrograph (SEM) cross-section showing the CAL 30 of the SOFC of Figure 1 in more detail. Microstructure is generally consistent throughout main part of the CAL 30 and there is good adhesion to adjacent layers. The porosity and grain sizes are consistent across the depth of the CAL 30. Densification occurs at the interface with interfacial air electrode layer of ReSC/ CGO.

Figure 3 illustrates mean cell potential as a function of temperature of cells with an CAL comprising a material according to the disclosure (curve 4) sintered at 870 °C (under the conditions 133 mAcm⁻², 75% Uf, 545°C reformat equilibrium) compared to standard cells (curve 5) in the same stack. The performance of Li-containing PSmO10 CAL cells is much better than standard cells, particularly at low temperatures.

Figure 4 illustrates mean cell potential as a function of temperature of cells with an CAL comprising a material of 2%Li-containing PSmO10 according to the disclosure (curve 6) sintered at 870°C, (under the conditions 225 mAcm⁻², 75% Uf, 545°C reformat equilibrium), compared to standard cells (curve 7) in the same stack. Li-containing PSmO10 CAL has a
5 very high mean cell voltage at 570 °C under these conditions of 0.867 V.

In order to investigate an operating stack (being operated in SOFC mode in this instance), the stack was supplied with a fuel mixture simulating partially externally steam-reformed natural gas, at a flow rate such that 75% of the oxidisable fuel was consumed by the electrochemical reaction within the stack. Air was supplied to the air electrode side of the stack at a flow-rate
10 well in excess of the stoichiometric requirement for oxygen, in order to minimise internal temperature gradients. There was a constant current density of 133 mAcm⁻² or 225 mAcm⁻². The stack temperature was varied by controlling the temperature of the furnace in which the test was being undertaken.

There follows in the Examples a general method for synthesizing Li-containing rare earth
15 doped praseodymia according to the invention (Example 1, 2 and 3), synthesising a printable ink using such Li-containing praseodymium powder (Example 4) and using such an ink to print a CAL (Example 5).

Example 1: Synthesis of Rare Earth (RE) doped praseodymium oxide powder

20 Solution preparation

A stoichiometric mixture of praseodymium nitrate hexahydrate and the desired RE dopant nitrate are dissolved in deionised (DI) water to give a solution molarity of 0.4M.

In a separate container under a fume hood, oxalic acid dihydrate is dissolved in the same volume of DI water used to dissolve the nitrates to give a molar ratio of oxalic acid to nitrates
25 of 1.7 (slightly in excess of the stoichiometric requirement of 1.5 to ensure all the metal ions precipitate).

Once the oxalic acid fully dissolves, concentrated ammonium hydroxide solution is added whilst monitoring the pH, until the acid has been neutralised (pH 7) leaving a solution of ammonium oxalate.

30 Precipitation

Whilst vigorously stirring the mixture, the solution of nitrates is added to the ammonium oxalate solution, resulting in a pale green precipitate of insoluble praseodymium plus dopant oxalate.

Filtration

- 5 A Buchner funnel with a high-strength filter paper and aquarium pump is prepared. With the pump running, the precipitate mixture is poured onto the filter and sufficient time was allowed to pass until most of the supernatant solution has been removed, leaving a cake of precipitate on the filter paper.

Washing

- 10 The precipitate is washed 3 times with DI water, then once with ethanol.

Drying

The wet filter cake is transferred from the funnel to suitable containers and dried in a solvent-rated oven overnight at 70 °C.

Pulverisation

- 15 The dried precipitate cake is pulverised using a pestle and mortar, then the resulting powder is transferred to alumina crucibles.

Example 2: Alternative synthesis of RE doped praseodymium oxide powder

Solution preparation

- 20 A stoichiometric mixture of praseodymium nitrate hexahydrate and the desired RE dopant nitrate are dissolved in deionised (DI) water to give a solution molarity of 0.15M.

In a separate container under a fume hood, concentrated ammonium hydroxide solution is diluted in DI water to give a 0.45M solution of the same volume as the nitrate solution.

Precipitation

- 25 Whilst vigorously stirring the mixture, the solution of nitrates is added to the ammonium hydroxide solution, resulting in a pale green gelatinous precipitate of insoluble praseodymium plus dopant hydroxide.

Filtration

- A Buchner funnel with a high-strength filter paper and aquarium pump is prepared. With the pump running, the precipitate mixture is poured onto the filter and sufficient time was allowed to pass until most of the supernatant solution has been removed, leaving a cake of precipitate on the filter paper.

Washing

The precipitate is washed 3 times with DI water, then once with ethanol.

Drying

- The wet filter cake is transferred from the funnel to suitable containers and dried in a solvent-rated oven overnight at 70 °C.

Pulverisation

The dried precipitate cake is pulverised using a pestle and mortar, then the resulting powder is transferred to alumina crucibles.

- 15 Example 3: Infiltration of source of lithium in the RE doped praseodymium oxide powder

Samples of co-precipitated RE doped praseodymium oxide powder were obtained for use in the subsequent procedure. The samples were contacted with a source of lithium according to the following method.

- 20 Samples of 10% Sm praseodymium oxide ($\text{Pr}_{0.9}\text{Ln}_{0.1}\text{O}_{(1.95-\delta)}$, “PSmO10”) were treated to produce two compositions with 1 and 2 cation% lithium.

0.5 M lithium nitrate solution in ethanol was added slowly to PSmO10 powder using a high precision pipette, ensuring the powder never became visibly wet. The resultant powder was then mixed in pestle and mortar.

- 25 The Li-containing PSmO10 powder was oven dried and then calcined at 500 °C for 2h to decompose the lithium nitrate to lithium oxide.

Samples of PSmO10, 1 cation% Li-containing PSmO10 and 2 cation% Li-containing PSmO10 were calcined in a tube furnace at 850 °C for 1h to simulate cathode firing.

Pellets made of the same powders were uniaxially pressed and fired at the same time to evaluate sintering.

Sintering shrinkage was evaluated and the results shown in Table 1, below.

5

<u>Lithium doping level</u>	<u>Linear shrinkage after 850°C firing/ %</u>
Undoped	0.77
1 cation%	0.85
2 cation%	2.69

Table 1. Sintering shrinkage evaluation.

Example 4: Synthesis of a Printable Ink

10 Dispersal and milling of Li-containing RE-doped praseodymium oxide powder

Li-containing RE-doped praseodymium oxide powder, manufactured as discussed in Examples 1 to 3, is weighed out and mixed with a carrier, a dispersant and an anti-foaming agent to form a slurry comprising a target amount of about 46 wt% powder.

15 The slurry is transferred to a basket mill to which double the weight of slurry of 1mm YSZ milling media are also added.

The slurry is milled at around 7000 rpm until a $d_{90} < 0.9\mu\text{m}$ was achieved. The particle size distribution may be measured using a Malvern Mastersizer® 2000 laser diffraction particle size analyser.

The slurry is then removed from the basket mill.

20 Ink manufacture

The dispersed and milled Li-containing RE-doped praseodymium oxide powder slurry made in the preceding section is transferred to small high-shear disperser (HSD) pot and placed on the HSD.

Binder powder in an amount corresponding to 2.5-3.5wt% of finished ink is weighed out.

- 5 The binder is added to slurry being actively dispersed on the HSD.

The ink is left on the HSD until the binder fully dissolves in the ink.

The ink is transferred to a triple roll mill (TRM) for final homogenisation and passed through the mill four times with a front nip of 5µm, ensuring the binder is fully homogenised into the ink and that no particles bigger than 5µm remain in the finished ink.

10

Example 5: Printing the Ink and forming the active layer

The substrate for printing comprised electrolyte layers deposited on a metal-supported SOFC.

The ink was screen printed, using an automated screen printer, as a single pass onto the electrolyte layers of the metal-supported SOFC. It was then dried in a drying oven. The

- 15 combination of ink solids content and screen mesh was chosen to give a thin print of approximately 3µm. Following addition of a CBL, the layer was then sintered together with the CBL at a temperature from 820 to 870 °C to form the CAL. Following sintering, x-ray diffraction and BET analysis was repeated. Post-sintering, there was a slight increase in crystallite size and a reduction in BET surface area, but no change in the crystal structure.

- 20 The layer still consisted of a single phase having a cubic fluorite structure.

Example 6: SOFC Cells using an Air Electrode CAL of Li-containing PrLnO.

Li-containing RE-doped praseodymium oxide powder slurry as described herein and exemplified in Examples 1 to 4 above, has equivalent or better performance than standard.

- 25 SOFC air electrodes consisting of three layers were produced. The three-layer electrode advantageously reduces the effect of chromium contamination (praseodymium oxide may react with chromia to form a perovskite) and ensures even better adhesion between the bulk layer and the active layer.

The three layers of the electrode were a bulk layer of LCN60 offering excellent stability and thermal expansion matching to the rest of the cell, an interfacial composite layer of rare-earth strontium cobaltite/ CGO and a catalytically active layer of rare-earth doped praseodymium oxide. The interfacial layer both ensures good adhesion between the active layer and the bulk and acts as a poison getter for the active layer as poisons such as chromium and sulphur will react with the rare earth strontium cobaltite/ cobalt ferrite before getting to the strontium free active layer (which may be susceptible to chromium poisoning). The interfacial layer has a similar thermal coefficient to the air electrode bulk layer. This protects the active layer from degradation (which would not be affected by water vapour, carbon dioxide or sulphur dioxide)

The air electrode was produced by being screen printed as three layers, a thin layer (ca 3 microns) of the first electrode material (e.g. 2 cation % Li PSmO10), a thin layer (ca 3 microns) of rare earth strontium cobaltite/ CGO (e.g. ReSC/ CGO10 60:40; wherein "Re" refers to rare earth), and finally a much thicker (ca 40 microns) of bulk layer (LCN60).

Optionally these layers may be burnt out and isostatically or uniaxially pressed to enhance their green density, and then finally sintered in air at 800-900 °C to form the finished air electrode.

Air electrodes as described were provided in standard metal supported SOFCs and incorporated in 17 cell stacks. For each cell the anode was ceria-nickel cermet and the electrolyte comprised CGO with a doped zirconia electron blocking layer. The CAL may be directly in contact with the zirconia electron blocking layer or a layer of e.g. CGO may be interposed between the active layer and the zirconia electron blocking layer.

The stack may be run with air flow on the air side and fuel of simulated steam-reformed natural gas on the fuel side under the conditions described above.

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 electrode for an electrochemical cell, the electrode comprising at least a first layer comprising a first electrode composition, the first electrode composition comprising $\text{Pr}_{(1-x)}\text{Ln}_x\text{O}_{(2-0.5x-\delta)}$ and a source of lithium,

wherein Ln is selected from at least one rare earth metal selected from La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y and mixtures thereof,

δ is the degree of oxygen deficiency, and

$$0.01 \leq x \leq 0.4.$$

10

2. An electrode according to claim 1, wherein the source of lithium is present in the first electrode composition in an amount of 0.001 to 5 cation %.

3. An electrode according to claim 2, wherein the source of lithium is present in the first electrode composition in an amount of 0.01 to 5 cation %.

4. An electrode according to any one of the preceding claims, wherein the rare earth metal is selected from La, Sm, Gd, and Yb; preferably Sm.

5. An electrode according to any one of the preceding claims, wherein $0.02 \leq x \leq 0.25$.

6. An electrode according to any one of the preceding claims, wherein the first electrode composition comprises $\text{Pr}_{0.9}\text{Ln}_{0.1}\text{O}_{(1.95-\delta)}$, $\text{Pr}_{0.85}\text{Ln}_{0.15}\text{O}_{(1.925-\delta)}$, $\text{Pr}_{0.8}\text{Ln}_{0.2}\text{O}_{(1.9-\delta)}$ or mixtures thereof, and a source of lithium.

25

7. An electrode according to any one of the preceding claims, wherein the first layer comprises 20% by weight or greater of the first electrode composition; optionally 30% by

weight or greater of the first electrode composition; optionally 40% by weight or greater of the first electrode composition; optionally 55% by weight or greater of the first electrode composition.

- 5 8. An electrode according to any one of the preceding claims, wherein the first layer has a thickness in the range 1 μm to 7 μm .
9. An electrode according to any one of the preceding claims, wherein the electrode comprises at least a second layer comprising a second electrode material.
- 10
10. An electrode according to any one of the preceding claims, wherein the electrode is an air electrode.
11. An electrode according to any one of the preceding claims, wherein the source of
- 15 lithium comprises lithium oxide, lithium hydroxide, a lithium salt, lithium salt of an organic acid and/or lithium as a dopant.
12. An electrochemical cell comprising an electrode according to any one of the preceding claims; optionally further comprising one or more of: an electrolyte, a second fuel
- 20 electrode, and a substrate.
13. An electrochemical cell according to claim 12, wherein the electrochemical cell further comprises an electrolyte and the electrolyte comprises at least one electrolyte layer comprising doped ceria, optionally selected from samarium-doped ceria (SDC), gadolinium-
- 25 doped ceria (GDC), praseodymium doped ceria (PDC), samaria- gadolinia doped ceria (SGDC) and mixtures thereof.

14. An electrochemical cell according to either claim 12 or claim 13, wherein the electrochemical cell is an electrolyser cell, an oxygen separator, a sensor or a fuel cell, and optionally, wherein the electrochemical cell comprises a solid oxide electrochemical cell.

5 15. A method of producing an electrode for an electrochemical cell, the method comprising:

providing a substrate, optionally having deposited thereon layers comprising a fuel electrode and an electrolyte,

10 applying at least a first layer comprising a first electrode composition, the first electrode composition comprising $\text{Pr}_{(1-x)}\text{Ln}_x\text{O}_{(2-0.5x-\delta)}$ and a source of lithium,

optionally drying at least said first layer, and

optionally sintering the at least said first layer;

thereby forming an electrode;

15 wherein Ln is selected from at least one rare earth metal selected from La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y and mixtures thereof,

δ is the degree of oxygen deficiency, and

$0.01 \leq x \leq 0.4$.

16. A method as claimed in claim 15, wherein the method further comprises

20 applying material to the substrate to form at least one electrolyte layer,

applying the first electrode composition on the electrolyte layer to form an air electrode layer,

optionally drying said air electrode layer, and

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

25

17. A method as claimed in either claim 15 or claim 16, wherein sintering or co-sintering is conducted at a temperature in the range 750 °C to 900 °C.

18. A method as claimed in any one of claims 15 to 17, wherein the first electrode composition comprises $\text{Pr}_{(1-x)}\text{Ln}_x\text{O}_{(2-0.5x-\delta)}$ and a lithium salt, preferably lithium nitrate.
- 5 19. A method as claimed in any one of claims 15 to 18, further comprising a step of preparing the first electrode composition by mixing $\text{Pr}_{(1-x)}\text{Ln}_x\text{O}_{(2-0.5x-\delta)}$ and a source of lithium, optionally a source of lithium dissolved or dispersed in a solvent, optionally an alcohol.
20. A composition comprising $\text{Pr}_{(1-x)}\text{Ln}_x\text{O}_{(2-0.5x-\delta)}$ and a source of lithium,
- 10 wherein Ln is selected from at least one rare earth metal selected from La, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, Y and mixtures thereof,
- δ is the degree of oxygen deficiency, and
- $0.01 \leq x \leq 0.4$.
- 15 21. A composition comprising $\text{Pr}_{(1-x)}\text{Sm}_x\text{O}_{(2-0.5x-\delta)}$ and a source of lithium,
- wherein δ is the degree of oxygen deficiency, and
- $0.01 \leq x \leq 0.4$.
22. A stack of electrochemical cells as claimed in any one of claims 12 to 14.