Ionic/Electronic Conductivity, Thermal/Chemical Expansion and Oxygen Permeation in Pr and Gd Co-Doped Ceria Pr_xGd_0.1Ce_0.9-xO_1.95-

Cheng, Shiyang; Chatzichristodoulou, Christodoulos; Søgaard, Martin; Kaiser, Andreas; Hendriksen, Peter Vang

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Ionic/Electronic Conductivity, Thermal/Chemical Expansion and Oxygen Permeation in Pr and Gd co-doped ceria Pr$_x$Gd$_{0.1}$Ce$_{0.9-x}$O$_{1.95-\delta}$

Shiyang Cheng*, Christodoulos Chatzichristodoulou, Martin Søgaard, Andreas Kaiser and Peter Vang Hendriksen*

* Corresponding authors: cheng_shiyang@foxmail.com and pvhe@dtu.dk

Department of Energy Conversion and Storage, Technical University of Denmark, DTU Risø campus, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

Abstract

The oxygen permeation flux of Ce$_{0.9}$Gd$_{0.1}$O$_{1.95-\delta}$ (CGO)-based oxygen transport membranes under oxidizing conditions is limited by the electronic conductivity of the material. This work aims to enhance the bulk ambipolar conductivity of CGO by partial substitution of Ce with the redox active element Pr. A series of compositions of Pr$_x$Gd$_{0.1}$Ce$_{0.9-x}$O$_{1.95-\delta}$ ($x=0, 0.02, 0.05, 0.08, 0.15, 0.25, 0.3$ and $0.4$) was prepared by solid state reaction. X-ray powder diffraction (XPD) indicates that Pr is completely dissolved in the fluorite structure up to 40 at.%. Pronounced nonlinear thermal expansion behaviour was observed as a function of temperature, due to the simultaneous contributions of both thermal and chemical expansion. The electronic and ionic conductivities were measured as a function of temperature and oxygen partial pressure. Within the range from 10 to 15 at.% Pr, a drastic drop of the activation energy of the hole mobility and an abrupt increase of the hole conductivity at low temperature was observed. The behaviour could be rationalized by a simple percolation model. Oxygen permeation fluxes through disk shaped samples fed with air on one side and N$_2$ on the other side were also measured. The oxygen flux through Pr$_{0.05}$Gd$_{0.1}$Ce$_{0.85}$O$_{1.95-\delta}$ was higher than that for CGO by one order of magnitude owing to the enhanced electronic conductivity albeit the flux is still limited by the
electronic conductivity. In terms of the electronic and ionic conductivity, the estimated maximum oxygen permeation flux of a 10 μm Pr$_{0.4}$Gd$_{0.1}$Ce$_{0.9}$O$_{1.95-δ}$-based membrane exceeds 10 Nm$^2$min$^{-1}$ at 900 °C under a small oxygen potential gradient (0.21/10$^{-3}$ bar) which is promising for use in oxygen production and in oxy-fuel combustion. Also the material may be well applicable to SOFC/SOEC composite electrodes where mixed conductivity is also desirable.

**Key words:** Pr/Gd co-doped ceria; oxygen transport membranes; electronic conductivity; ionic conductivity; percolation model; SOFC/SOEC electrodes
1. Introduction

Dense ceramic oxygen transport membranes (OTMs) could potentially be applied for production of high purity oxygen for medical purposes, supply of oxygen in the steel industry, oxy-fuel combustion schemes, as well as in the cement and glass industries. Also, importantly, OTMs can beneficially be integrated with a biomass gasifier, allowing production of syngas (CO and H₂), which is a precursor for a variety of high value chemical products (1).

Besides being applicable for OTMs (2), acceptor doped-ceria has been intensively studied for use in a number of other applications e.g. solid oxide fuel cells (SOFCs) (3), solid oxide electrolysis cells (SOECs) (4) and for electrocatalysis (5). In particular, acceptor doped ceria (e.g. CGO) is interesting owing to high oxide ion conductivity (0.12 S cm⁻¹ for Gd₀.₁Ce₀.₉O₁.₉₅ at 900 °C (6)), appreciable electrocatalytic activity, high electronic conductivity under reducing conditions, and excellent chemical stability under harsh reducing and even corrosive gaseous conditions (3, 7). Kaiser et al. (8) reported that the oxygen permeation flux of a 27 μm asymmetric 10 at.% Gd-doped ceria-based membrane exceeds 10 N ml cm⁻² min⁻¹ under a gradient of air/H₂ at 850 °C (9), which is promising for applications provided that sufficient lifetime can be achieved. However, the ambipolar conductivity of ceria is relatively low when only mildly reducing conditions are imposed because of the low electronic conductivity under these conditions (<1×10⁻³ S cm⁻¹ at 900 °C in air (10)). The low electronic conductivity also results in the slow oxygen surface exchange rate (11, 12), which further limits the achievable oxygen flux. To provide technologically relevant oxygen fluxes for high pO₂ applications, such as production of pure oxygen and in oxy-coal combustion conditions, the electronic conductivity of CGO needs to be enhanced preferably to a value close to that of the ionic conductivity so that ambipolar conductivity can be maximized.
Doping redox active elements is a feasible strategy to enhance the electronic conductivity of ceria (13-18). Among rare earth elements, Praseodymium (Pr) and Terbium (Tb) show significant redox activity under mildly reducing conditions ($pO_2 = 1 \times 10^{-8}$-1 bar). Upon the reduction of Pr and Tb, electrons can migrate between the trivalent and tetravalent Pr/Tb, giving rise to an enhanced electronic conductivity. For instance, the $p$-type electronic conductivity of 3 at.% Pr-doped Gd$_{0.2}$Ce$_{0.8}$O$_{1.9-\delta}$ is enhanced by approximately 10 times relative to pure CGO in the temperature range from 600 °C to 750 °C (13). The electronic conductivity of Tb and Pr dual-doped ceria can be modified by changing the ratio between the two dopants: higher relative amount of Pr yields higher electronic conductivity, but leads to larger chemical expansion (16). Chatzichristodoulou et al. (16) and Bishop et al. (19) also found that doping Pr in ceria induces large chemical expansion, which will affect the thermomechanical stability of the material. It is thus of importance to examine the possible existence of an optimum amount of Pr in ceria that ensures satisfactory thermomechanical stability along with sufficient electronic conductivity.

When dissolved in the ceria lattice, Pr exists in two valence states (16). Upon increasing $pO_2$ and decreasing temperature, the concentration of Pr$^{4+}$ increases, accompanied by a decrease of oxygen vacancy concentration ($2Pr^{3+}_{Ce} + 1/2O_2 + V'^{**}_O = 2Pr^{4+}_{Ce} + O^{2-}_O$). In order to achieve, simultaneously, considerable oxygen vacancy and electron hole concentrations, various concentrations of Pr were doped in Gd$_{0.1}$Ce$_{0.9}$O$_{1.95-\delta}$ (partial Pr-substitution for Ce) and the effects were studied. Considerable oxygen vacancy concentration is expected in order to compensate the charge of the aliovalent dopants $Gd^{2+}_{Ce}$ and $Pr^{3+}_{Ce}$. The influence of dopant concentration on the electronic and ionic conductivity was investigated using ion-blocking Hebb-Wagner polarization in conjunction with electrochemical impedance spectroscopy. Also
effects on the achievable oxygen permeation fluxes were addressed to assess the potential of these materials for OTMs.

2. Theoretical consideration

In Pr\textsubscript{3}Gd\textsubscript{0.1}Ce\textsubscript{0.9-x}O\textsubscript{1.95-δ}, oxygen vacancies are formed to compensate effectively negatively charged Gd\textsuperscript{3+}, Pr\textsuperscript{3+} and Ce\textsuperscript{3+} that partially substitute Ce\textsuperscript{4+}. Assuming ideal behaviour for the reduction of Pr and Ce in the lattice (invariant values of reaction entropies and enthalpies), the expected defect reactions and mass action laws are:

\begin{equation}
Gd_xO_y \xrightarrow{Ce\textsubscript{Ce}} 2Gd\textsubscript{Ce}^+ + V\textsubscript{O}^{**} + 3O\textsubscript{O}^x
\end{equation}

\begin{equation}
2Pr\textsubscript{Ce}^x + O\textsubscript{O}^y \xleftrightarrow{} 2Pr\textsubscript{Ce}^+ + V\textsubscript{O}^{**} + 1/2O\textsubscript{O}^z (g)
\end{equation}

\begin{equation}
K_{Pr} = \exp \left( -\frac{\Delta H_{Pr}^0 - T\Delta S_{Pr}^0}{RT} \right) = \frac{P_{O_2}^{1/2} \left[V\textsubscript{O}^{**}\right] \left[Pr\textsubscript{Ce}^+\right]^2}{\left[O\textsubscript{O}^s\right] \left[Pr\textsubscript{Ce}^x\right]^2}
\end{equation}

\begin{equation}
2Ce\textsubscript{Ce}^x + O\textsubscript{O}^y \xrightarrow{} 2Ce\textsubscript{Ce}^+ + V\textsubscript{O}^{**} + 1/2O\textsubscript{O}^z (g)
\end{equation}

\begin{equation}
K_{Ce} = \exp \left( -\frac{\Delta H_{Ce}^0 - T\Delta S_{Ce}^0}{RT} \right) = \frac{P_{O_2}^{1/2} \left[V\textsubscript{O}^{**}\right] \left[Ce\textsubscript{Ce}^+\right]^2}{\left[O\textsubscript{O}^s\right] \left[Ce\textsubscript{Ce}^x\right]^2}
\end{equation}

Mass and site balances and electroneutrality requires:

\begin{equation}
\left[Ce\textsubscript{Ce}^x\right] + \left[Pr\textsubscript{Ce}^x\right] + \left[Gd\textsubscript{Ce}^x\right] = 2\left[V\textsubscript{O}^{**}\right]
\end{equation}

\begin{equation}
\left[Ce\textsubscript{Ce}^x\right] + \left[Pr\textsubscript{Ce}^x\right] + \left[Gd\textsubscript{Ce}^x\right] + \left[Ce\textsubscript{Ce}^+\right] + \left[Pr\textsubscript{Ce}^+\right] = 1
\end{equation}

\begin{equation}
\left[Pr\textsubscript{Ce}^x\right] + \left[Pr\textsubscript{Ce}^+\right] = x
\end{equation}

\begin{equation}
\left[V\textsubscript{O}^{**}\right] + \left[O\textsubscript{O}^s\right] = 2
\end{equation}

\begin{equation}
\left[Gd\textsubscript{Ce}^x\right] = 0.1
\end{equation}

Under oxidizing conditions, where \left[Ce\textsubscript{Ce}^x\right] \ll \left[Ce\textsubscript{Ce}^+\right], the coexistence of Pr\textsubscript{Pr} and Pr\textsubscript{Pr} leads to p-type electronic conductivity (20, 21). Assuming the reduction of cerium under oxidizing conditions to be negligible, the variation in oxygen non-stoichiometry (δ) (arising from redox of Pr only) can be calculated by the following equation:
The equilibrium constant for the reduction reaction of Pr can be obtained by fitting Eq. 11 to oxygen nonstoichiometry vs. $p_{O_2}$ data (at high $p_{O_2}$, $p_{O_2}>1\times10^{-4}$ bar), as will be shown in 4.4.

3. Experimental

3.1. Sample preparation and phase identification

The specimens in this work were synthesized by solid state reaction. Stoichiometric amounts of precursors of Ce(NO$_3$)$_3$·6H$_2$O (Sigma Aldrich 99.99%), Gd$_2$O$_3$ (Alfa Aesar 99.9%), Pr$_6$O$_{11}$ (Alfa Aesar 99.9%) and Co$_3$O$_4$ (Alfa Aesar 99.9%, for cobalt containing samples) were mixed by ball milling in ethanol for 24 hours. The resultant mixed powders were dried at 80°C for 10 hours and subsequently calcined at 1000 °C for 5 hours. The calcined powders were then uniaxially cold pressed at 400 MPa followed by isostatic pressing at 600 MPa. Cobalt-containing and cobalt-free pellets were sintered at 1200 °C and 1600 °C for 10 hours, respectively.

The crystal structures of the material (crushed sintered pellets) were characterized by X-ray powder diffraction (XRD). The XRD patterns were obtained with Cu Kα radiation using a Bruker Robot operating in Bragg-Brentano geometry in the $2\theta$ range from 20° to 90°. The obtained XRD patterns were indexed with the ICCD (International Centre for Diffraction Data) database by means of the software named DIFFRAC plus. Scanning electron microscopy (SEM) was carried out on a FE-SEM Zeiss Supra 35 electron microscope using an acceleration voltage of 15 kV.

3.2. Thermogravimetry
Thermogravimetric analysis (TGA) was performed using a Netzsch STA 409CD thermogravimeter and a Netzsch TG 439 thermal balance. The samples were prepared by uniaxially pressing the powder into pellets at a pressure of 400 MPa in a capillary die (φ = 0.5 cm). Porous samples were obtained by sintering the green sample at 1000 °C for 3 hours at heating and cooling rate of 2 °C min⁻¹. Buoyancy effects were corrected for by measuring the mass change of an Al₂O₃ powder sample with the same volume under the same conditions.

3.3. Dilatometry

Dilatometry measurements were performed using a differential contact dilatometer (DIL 402CD, NETZSCH GmbH, Germany). The samples were rectangular bars with a dimension of 1×1×10 mm³. An Al₂O₃ reference with a similar dimension was tested simultaneously with the sample. The heating rate was kept at 3 °C min⁻¹ to a final temperature of 1000 °C. All the measurements were conducted in air with a total gas flow of 50 ml min⁻¹ controlled by a mass flow controller.

3.4. Impedance spectroscopy

The total conductivity of each specimen was measured by Electrical Impedance Spectroscopy (EIS). Prior to the electrical measurements, symmetric (La₀.₆Sr₀.₄)₀.₉₉CoO₃₋δ (LSC) electrodes were screen printed on both sides of a 1-mm thick polished pellet (φ = 10 mm), followed by sintering at 1000 °C for 2 hours to obtain good adhesions between the specimen and the electrodes. The LSC electrodes were then covered with Pt layers (current collector) by hand painting to eliminate any contact resistance. EIS was carried out in the temperature range from 600 °C to 900 °C using a Solartron 1260 impedance spectrometer within the frequency range from 3 MHz down to 0.1 Hz under a fixed fluctuation voltage of 20 mV. Impedance spectra were plotted and fitted by the software package “Z-view” and “Z-plot”. The specimens were placed in a closed alumina chamber in which oxygen partial pressure was varied and monitored.
by controlling the flow of air and nitrogen by mass flow controllers. The oxygen partial pressure around the samples was measured by a zirconia-based sensor placed in close proximately to the sample.

3.5. Microelectrode ion-blocking Hebb-Wagner polarization measurements

The electronic conductivity of each sample was measured by means of a microelectrode ion-blocking Hebb-Wagner polarization method. Prior to the measurements, 1-mm thick dense circular samples (ø =10mm) were polished by SiC #300 sand papers, followed by further polishing using SiC #1000 and #1600 sand papers. The Hebb-Wagner measurement cell is schematically illustrated in Fig. 1. Similar setups have been used in a number of papers in the past (13, 22-25). A Pt microelectrode with a contact radius of 100-500 μm was placed on the sample under an external load. The periphery of the Pt microelectrode was sealed with a customized glass sealant (MgO/sodium aluminosilicate glass composites, 30/70 vol. %). The Hebb-Wagner cell was sandwiched with two Pt current collectors. The whole cell was finally placed inside a furnace in which the oxygen partial pressure was maintained at 0.21 atm by flowing 100 ml min⁻¹ of air. The cell was initially heated up to 950 °C at the rate of 1 °C min⁻¹ to soften the glass sealant, followed by cooling down to 750 °C at the same rate to achieve a gas tight solidified glass. The polarization measurement was then performed by stepwise varying voltage in 25 mV steps in the range from -800 to 200 mV. The steady state was achieved by dwelling for 12 minutes (more than 100 times the theoretical time needed to reach the steady state) in each step. The oxygen partial pressure in the vicinity of the microelectrode can be calculated by the Nernst equation:

\[
a_{O_2,\text{micro}} = a_{O_2,\text{ref}} \exp\left(\frac{4FV}{RT}\right) \tag{12}
\]
where $a_{O_2,\text{micro}}$ and $a_{O_2,\text{ref}}$ is the oxygen activity near the microelectrode and reference electrode, respectively. $V$ is the polarization voltage applied on the microelectrode relative to the reference/counter electrode. The sum of electron and electron hole conductivity in the vicinity of the ion-blocking microelectrode can, under a set of assumptions (13, 24, 26), be calculated in terms of the derivative of the steady state I-V curve:

$$\frac{\partial I}{\partial V} = 2\pi r_c \left( \sigma_e + \sigma_h \right) \quad (13)$$

where $r_c$ is the radius of the spherical microelectrode. If the micron-sized contact is circular rather than spherical, the factor $2\pi r_c$ is replaced by $4r_c$ (24).

**Fig. 1** (a) Schematic illustration and (b) image of the Hebb-Wagner polarization setup.

### 3.6. Oxygen permeation measurements

Oxygen permeation measurements were performed in the customized test configuration displayed in Fig. 2. Before the flux measurements, circular samples ($\approx 12$ mm) were polished by SiC #500 sand papers to achieve a thickness of approximately 1 mm. To mitigate the effect
of slow surface exchange, a highly porous circular La$_{0.6}$Sr$_{0.4}$CoO$_3$-$\delta$ (LSC)-based catalytic layer ($\varnothing \approx 5$ mm) was applied on the dense samples by screen printing with a LSC-based ink. The as-prepared catalytic layers were then calcined at 900°C for 1 hour to obtain good adhesion with the membrane surface. The area covered with the catalytic layer is ~0.8 cm$^2$.

The samples were sealed between two alumina tubes using a 30/70 vol.% mixture of a MgO and sodium aluminosilicate glass. The feed side tube below the membrane was supplied with gas from the feed side manifold, which featured a feed gas inlet and outlet. Similarly, the permeate side of the membrane was purged with gas from a “permeate side” manifold. The feed side was flushed with air with a constant flow rate of 100 Nml min$^{-1}$, and the permeate side was flushed at various flow rates of N$_2$ (from 30 to 300 Nml min$^{-1}$). All gas flows were measured by mass flow controllers. The net oxygen permeation flux can be deduced from the $p$O$_2$ difference between inlet and outlet gases. The $p$O$_2$ was monitored by two customized YSZ-based oxygen sensors. The total leak in the system was assessed by means of a mass flow meter on the permeate stream. When perfect sealing is achieved, the outlet gas flow rate is equivalent to the inlet flow plus the flow of the permeated oxygen. If there are leaks in the membrane or pinholes or cracks in the glass encapsulation, the flow rate of the outlet gas will be lower than that of the inlet gas. Typically, when a significant leak is observed during the permeation measurement, a thermally activated increase in oxygen flux is not observed. In the data reported here, the inlet and outlet flows were identical (within 1% uncertainty) and a thermal activated oxygen permeation flux was observed, indicating close to perfect sealing. The maximum leak originating from pinholes in the sealant and from other sources of oxygen in the permeate flow through the membrane is estimated to be lower than 5% at low temperature (600°C) based on the gas sensor. Below 600°C a large leak appeared as a result of sealant failure driven by thermal expansion mismatch between membrane and manifold tubes.
Fig. 2. (a) Schematic illustration of the membrane test rig. (b) Local enlargement of the heated part of the membrane test rig.

4. Results

4.1. Sintering

Fig. 3 displays the microstructure of thermally etched samples of different composition. Table 1 summarizes the specific composition, sintering temperature (Ts), theoretical density, measured density, relative density and average grain size of the specimens analysed. The average grain size of the cobalt oxide free samples sintered at 1600 °C lies in the range from 2 to 5 μm, and shows a slightly increasing tendency with increasing Pr content. The cobalt oxide containing samples sintered at 1200 °C are completely dense with relatively small average grain size (200-500 nm). This elucidates that cobalt oxide serves as an effective sintering aid in of doped ceria, which is well in line with literature (27).
Fig. 3 Back-scattered SEM micrographs of polished and thermally etched surface of each sample. (scale bar=2µm)

Table 1. Sintering temperature, density and grain size of pure and Pr-doped CGO.

<table>
<thead>
<tr>
<th>Abbreviated name</th>
<th>Composition</th>
<th>Tₛ / °C</th>
<th>Theoretical density/ g cm⁻³</th>
<th>Measured geometrical density / g cm⁻³</th>
<th>Relative density %</th>
<th>d₉/µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGO</td>
<td>Gd₉₀Ce_{0.1}O₁.₉₅</td>
<td>1600</td>
<td>7.20</td>
<td>7.10</td>
<td>98.6</td>
<td>3.0±1.0</td>
</tr>
<tr>
<td>CPGO2</td>
<td>Pr₀.₀₂Gd₉₀Ce_{0.1}O₁.₉₅</td>
<td>1600</td>
<td>7.18</td>
<td>6.90</td>
<td>96.1</td>
<td>4.0±1.0</td>
</tr>
<tr>
<td>CPGO5</td>
<td>Pr₀.₀₅Gd₉₀Ce_{0.1}O₁.₉₅</td>
<td>1600</td>
<td>7.24</td>
<td>6.95</td>
<td>96.0</td>
<td>5.0±1.0</td>
</tr>
<tr>
<td>Cao2CPGO5</td>
<td>Co₀.₀₂Pr₀.₀₂Gd₉₀Ce_{0.1}O₁.₉₅</td>
<td>1200</td>
<td>7.24</td>
<td>7.02</td>
<td>97.0</td>
<td>0.2-0.5</td>
</tr>
<tr>
<td>Cao5CPGO5</td>
<td>Co₀.₀₅Pr₀.₀₅Gd₉₀Ce_{0.1}O₁.₉₅</td>
<td>1200</td>
<td>7.25</td>
<td>7.05</td>
<td>97.2</td>
<td>0.2-0.5</td>
</tr>
<tr>
<td>CPGO8</td>
<td>Pr₀.₀₂Gd₉₀Ce_{0.05}O₁.₉₅</td>
<td>1600</td>
<td>7.22</td>
<td>7.10</td>
<td>98.3</td>
<td>4.0±1.0</td>
</tr>
<tr>
<td>CPGO15</td>
<td>Pr₀.₀₁Gd₉₀Ce_{0.15}O₁.₉₅</td>
<td>1600</td>
<td>7.13</td>
<td>6.60</td>
<td>92.6</td>
<td>4.0±1.0</td>
</tr>
<tr>
<td>CPGO25</td>
<td>Pr₀.₀₂₅Gd₉₀Ce_{0.15}O₁.₉₅</td>
<td>1600</td>
<td>7.03</td>
<td>6.50</td>
<td>92.5</td>
<td>5.0±1.0</td>
</tr>
<tr>
<td>CPGO30</td>
<td>Pr₀.₀₅Gd₉₀Ce_{0.15}O₁.₉₅</td>
<td>1600</td>
<td>6.92</td>
<td>6.20</td>
<td>89.6</td>
<td>6.0±1.0</td>
</tr>
<tr>
<td>CPGO40</td>
<td>Pr₀.₀₅Gd₉₀Ce_{0.15}O₁.₉₅</td>
<td>1600</td>
<td>6.70</td>
<td>6.30</td>
<td>94.0</td>
<td>6.0±1.0</td>
</tr>
</tbody>
</table>

4.2. X-ray diffraction

XRD patterns of crushed dense pellets of PrₓGd₀.₁Ce₀.₉₋ₓO₁.₉₅₋ₓ (x=0.02, 0.05, 0.08, 0.15, 0.25, 0.3 and 0.4) and CoₓPr₀.₀₂Gd₀.₁Ce₀.₈₅O₁.₉₅₋ₓ (x=0.02 and 0.05) are shown in Fig. 4. Zero shifts were compensated for using an internal standard (LaB₆ powder). No significant shift of the (111) reflection was detected, indicative of an insignificant influence of the addition of the dopant on
the lattice parameter. No indication of secondary phases originating from side reactions or precipitation of insolvable dopants can be detected within the resolution limit of the XRD, indicating that the solubility limit of Pr in CGO is more than 40 at.%, which is in accordance with the solubility limit of 70 at.% reported by Taksu et al. (28) for partial Pr-substitution for cerium in Pr\(_x\)Ce\(_{1-x}\)O\(_{2-0.5x}\) at 1400 °C. Co\(_3\)O\(_4\) and CoO phases cannot be indexed from Co\(_x\)Pr\(_{0.05}\)Gd\(_{0.1}\)Ce\(_{0.85}\)O\(_{1.95-\delta}\) (x=0.05). Due to the high temperature (1200 °C) used to sinter cobalt-containing samples, cobalt oxide in this condition may likely react with trivalent Gd, Pr cations, forming slight amount of GdCoO\(_3\) or PrCoO\(_3\) phases whose the highest intensity peaks (2\(\theta\) ≈ 32°, PrCoO\(_3\) :PDF#25-1069 and GdCoO\(_3\) :PDF#25-1057) might be overwhelmed by the peak of (200) crystal plane from the main phase.

Fig. 4 Powder X-ray diffraction patterns of Pr\(_x\)Gd\(_{0.1}\)Ce\(_{0.9-x}\)O\(_{1.95-\delta}\) (x=0.02, 0.05, 0.08, 0.15, 0.25, 0.3 and 0.4) and Co\(_x\)Pr\(_{0.05}\)Gd\(_{0.1}\)Ce\(_{0.85}\)O\(_{1.95-\delta}\) (x=0.02 and 0.05). Inset: zoom corresponding to the (111) reflection in the 2\(\theta\) range from 27 to 30 degree.

4.3. Lattice parameter and microstructure
The lattice parameter obtained from XRD is shown in Fig. 5 along with calculated lattice parameters obtained by Kim’s empirical formula (29)

\[
a = 0.5413 + \sum_k (0.022 \Delta r_k + 0.00015 \Delta z_k) m_k \tag{14}
\]

where \(a\) is the unit cell parameter of the fluorite oxide at room temperature, \((\Delta r_k = r_k - r_h)\) is the difference in ionic radius of the kth dopant \((r_k)\) and the host cation \((r_h)\) in eight-fold coordination from Shannon’s compilation (30), \((\Delta z_k = z_k - z_h)\) is the valence difference between dopant and host, and \(m_k\) is the mole fraction of the kth dopant in the form of PrO\(_x\) (\(x=1.5/2\)).

As displayed in Fig. 5, the experimentally observed lattice parameter lies closer to the calculated values for Pr being tetravalent \((\text{Pr}^{4+})\) in the materials than when assuming \(\text{Pr}^{3+}\). McCullough reported that praseodymium is readily oxidized to \(\text{Pr}^{4+}\) in the presence of \(\text{Ce}^{4+}\) (31). This suggests that the concentration of tetravalent Pr prevails at room temperature in the Pr-doped CGO (slow cooling in air). Due to the similar ionic radii between \(\text{Pr}^{4+}\) (CN=VIII 0.96 Å (30)) and \(\text{Ce}^{4+}\) (CN=VIII 0.97 Å (30)), the lattice parameter does not vary significantly with increasing dopant concentration, which is similar to the trend observed in Pr-doped ceria (32). The lattice parameter of the Co-containing samples does not deviate from the Co-free comparable specimens. Lewis et al. (33) reported a similar result that the lattice constant of CGO is not influenced by the addition of cobalt oxide because the cobalt is effectively insoluble in the CGO lattice.
Fig. 5 Experimental and calculated lattice parameters vs. Pr concentration. Inset: lattice parameter vs. $x$ in $\text{Co}_{0.9}\text{Pr}_{0.05}\text{Gd}_{0.1}\text{Ce}_{0.9-x}\text{O}_{1.95-\delta}$.

4.4. Oxygen nonstoichiometry

Fig. 6 displays the oxygen nonstoichiometry data of the samples along with the best least square fit curves ($0.90<R^2<0.99$) using the ideal defect model (Eq. 11). In the investigated $p\text{O}_2$ regime (blue regime) the oxygen nonstoichiometry ($\delta$) increases with decreasing oxygen partial pressure until it reaches a plateau (at $\delta=x/2$), where all the Pr is trivalent. The equilibrium constants ($K_{\text{Pr}}$) at each temperature were obtained from the fit of the defect model to the data. The equilibrium enthalpy and entropy were obtained from the slope and intercept of the linear fit to the data of $-\ln(K_{\text{Pr}})$ vs. $1/T$ according to the equation:
The thermodynamic parameters thus deduced for each composition are summarized in Table 2. It is noteworthy that the enthalpy of reduction of Pr decreases with increasing Pr concentration, indicating a more facile reduction of Pr and release of oxygen with increasing Pr concentration or oxygen nonstoichiometry. Chatzichristodoulou et al. (16) also found that reduction is facilitated with increasing oxygen nonstoichiometry in Pr and Tb co-doped ceria. Stefanik et al. (34) also pointed out that the reduction enthalpy of Pr decreases with increasing Pr concentration, indicating higher Pr concentration gives rise to higher reducibility, which is consistent with the general trend observed in this work.

**Table. 2** The thermodynamic parameters for the reduction of Pr in CPGO15, CPGO25, CPGO30 and CPGO40.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta H_{Pr}$/kJ mol$^{-1}$</th>
<th>$\Delta S_{Pr}$/ J K$^{-1}$ mol$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPGO8</td>
<td>200±34</td>
<td>158±34</td>
<td>This work</td>
</tr>
<tr>
<td>CPGO15</td>
<td>204±25</td>
<td>156±24</td>
<td>This work</td>
</tr>
<tr>
<td>CPGO25</td>
<td>132±15</td>
<td>108±14</td>
<td>This work</td>
</tr>
</tbody>
</table>

**Fig. 6** Fit of the ideal defect model to the oxygen nonstoichiometry data of (a) CPGO8, (b) CPGO15, (c) CPGO25, (d) CPGO30 and (e) CPGO40 measured by TGA.
4.5. Thermal expansion

Thermal expansion curves of Pr$_x$Gd$_{0.1}$Ce$_{0.9-x}$O$_{1.95-\delta}$ measured on cooling the samples from 900 °C to room temperature in air are shown in Fig. 7(a). Below 400 °C, all the samples show linear expansion. The thermal expansion curves display a non-linear behaviour with an inflection point in the range from 500 °C to 600 °C, particularly for the samples with 15 at.% Pr or more. It is evident that Pr-doped CGO follows a similar tendency as Pr doped ceria where the strain increases with increasing Pr concentration in the specimen. The increased and highly non-linear apparent TEC in Pr-doped ceria is primarily ascribed to the chemical strain originating from the combination of slight contraction of the unit cell upon formation of oxygen vacancies and expansion of the unit cell upon partial reduction of Pr (16, 36). The total expansion (the measured quantity) is the sum of the thermal and the chemical expansion (stoichiometric expansion (37)), which can be written:

$$\varepsilon = \alpha \Delta T + \beta \Delta \delta$$  \hspace{2cm} (16)

where $\alpha$ is the thermal expansion coefficient (TEC), and $\beta$ is the stoichiometric expansion coefficient (37). Assuming a constant thermal and stoichiometric expansion coefficient (37) at a given oxygen partial pressure, the non-linear total expansion curve can be fitted by a linear thermal expansion curve and a nonlinear chemical expansion curve (Fig. 7b). Values of the thermal expansion and chemical stoichiometric expansion coefficients deduced from this type
of fitting are listed in Table 3. The chemical expansion coefficient is observed to decrease with increasing dopant concentration. For samples doped with similar Pr concentration (Pr$_{0.2}$Ce$_{0.8}$O$_{1.9-\delta}$ vs. CPGO25), the chemical expansion coefficients are very close. (0.084 mol$^{-1}$ for Pr$_{0.2}$Ce$_{0.8}$O$_{1.9}$ (16) and 0.08 mol$^{-1}$ for CPGO25). It should be noted that Eq. 16 applies in general to small perturbations; $\beta$ is best determined at constant temperature with a change in $\delta$ driven by varying pO$_2$, and $\alpha$ should be determined at fixed $\delta$. We did not conduct such differential measurements (isothermal dilatometry). In the analysis presented, leading to estimates of $\beta$ (Table 3), one assumes that the $\alpha$ value determined at low temperature (where changes $\delta$ in are small) is constant in the whole temperature range.

Fig. 7 (a) Thermal expansion curves for Pr$_x$Gd$_{0.1}$Ce$_{0.9-x}$O$_{1.95-\delta}$ in air. The strain of CPO20 is the data taken from (16). (b) Temperature dependence of oxygen nonstoichiometry, thermal expansion and estimated chemical expansion curve of CPGO40. c) estimated chemical expansion of CPGO as a function of temperature.

Table 3. Integrated thermal and expansion chemical expansion coefficients (200-900 °C)

<table>
<thead>
<tr>
<th>Abbreviated name</th>
<th>$\alpha_{int}$/ K$^{-1}$</th>
<th>$\alpha_{therm}$/ K$^{-1}$</th>
<th>$\beta$/ mol$^{-1}$ (600-900°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGO</td>
<td>12.5×10$^{-6}$</td>
<td>12.5×10$^{-6}$</td>
<td>n/a</td>
</tr>
<tr>
<td>CPGO2</td>
<td>13.2×10$^{-6}$</td>
<td>12.5×10$^{-6}$</td>
<td>n/a</td>
</tr>
<tr>
<td>CPGO5</td>
<td>13.8×10$^{-6}$</td>
<td>12.5×10$^{-6}$</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td>$10^{-6}$</td>
<td>$10^{-6}$</td>
<td>0.05</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>-----------</td>
<td>------</td>
</tr>
<tr>
<td>CPGO8</td>
<td>14.0</td>
<td>12.5</td>
<td>0.05</td>
</tr>
<tr>
<td>CPGO15</td>
<td>21.5</td>
<td>12.5</td>
<td>0.13</td>
</tr>
<tr>
<td>CPGO25</td>
<td>23.4</td>
<td>12.5</td>
<td>0.08</td>
</tr>
<tr>
<td>CPGO30</td>
<td>24.0</td>
<td>12.5</td>
<td>0.08</td>
</tr>
<tr>
<td>CPGO40</td>
<td>26.5</td>
<td>12.5</td>
<td>0.08</td>
</tr>
<tr>
<td>Pr$<em>{0.2}$Ce$</em>{0.8}$O$_{1.9-\delta}$ (16)</td>
<td>22.7</td>
<td>n/a</td>
<td>0.08</td>
</tr>
<tr>
<td>Tb$<em>{0.2}$Ce$</em>{0.8}$O$_{1.9-\delta}$ (16)</td>
<td>18.2</td>
<td>n/a</td>
<td>0.09</td>
</tr>
</tbody>
</table>

4.6. Electronic conductivity (blocking electrode measurement)

The contact area of the Pt microelectrode was determined using Newman’s formula (38)

$$r_c = \frac{1}{4R_s \sigma}$$  \hspace{1cm} (17)

where $r_c$ is the radius of the micro-electrode, $R_s$ is the serial resistance found from the intercept with the real axis at the high frequency of the impedance spectra and $\sigma$ is the conductivity of the sample. The contact radius thus determined was typically between 100 $\mu$m and 500 $\mu$m, in good agreement with ref. (24) where similar conditions were applied. The contact radius evaluated by impedance spectroscopy was as expected not sensitive to the temperature or oxygen partial pressure.

The plots of the steady state current density of CPGO8 measured in the blocking electrode geometry versus the potential at 700°C, 800°C and 900°C are presented in Fig. 8. A current plateau in the range of -0.4-0V is observed. Excellent coincidence of the branches recorded in the negative and positive polarization direction upon repeated cycles indicate that any hysteresis arising from creep of the Pt micro-electrode and/or sluggish equilibrium between the redox of
Pr$^{3+}$ and Pr$^{4+}$ is negligible, and accordingly confirms that the I-V curves are obtained in the steady state.

**Fig. 8** Steady state current voltage polarization curve at 700 °C, 800 °C and 900 °C using air at the reference Pt electrode.

### 4.7. Total and Electronic conductivity versus pO$_2$

The oxygen activity dependence of the partial electronic and total conductivity of each sample is presented in Fig. 9. The electronic conductivity of CGO measured in this work agrees well with the electronic conductivity of CGO reported by Chatzichristodoulou *et al.* (24). In general, the electronic conductivity of CPGO is dominated by n-type and p-type under low and high oxygen partial pressures, respectively. The minimum point at intermediate pO$_2$ corresponds to the transition from n-type to p-type conductivity. It is noteworthy that the minimum point shifts towards lower oxygen partial pressure with increasing Pr concentration.
Fig. 9 Logarithm of electronic (open symbols) and total conductivity (half filled) of \( \text{Pr}_x\text{Gd}_{0.1}\text{Ce}_{0.9-x}\text{O}_{1.95-\delta} \) \( (x=0, 2, 5, 8, 15, 25, 30\) and \(40) \) versus \( \log \rho_0 \) at 900 °C, 800 °C and 700 °C.

In contrast to the electronic conductivity of CGO which follows a typical relationship of

\[
\sigma = \sigma_n^0 \rho_0^{-\frac{1}{4}} \theta + \sigma_p^0 \rho_0^{\frac{1}{4}},
\]

the electronic conductivity of CPGO possesses a more varied \( \rho_0 \) dependency. The slope of the n-type electronic conductivity of slightly doped samples (CPGO2, CPGO5, CPGO8 and CPGO15) at low \( \rho_0 \) approaches \(-\frac{1}{4}\), whereas for the heavily doped samples (CPGO25, CPGO30 and CPGO40) the slope is depressed especially at low temperature.

Under oxidizing conditions, the slopes vary within the range from \(\frac{1}{4}\) to \(\frac{1}{8}\), in agreement with ref. (13). Evidently, the p-type electronic conductivity strongly increases with increasing Pr concentration. In particular for CPGO40, the p-type electronic conductivity is higher than that.
of CGO by two orders of magnitude at 700 °C. The observed enhancement of p-type conductivity upon Pr substitution is in line with previous literature (13, 16, 39, 40). It is also seen that the electronic conductivity becomes insensitive to the temperature for these heavily doped samples (>15 at.%), which coincides with previous findings by Chatzichristodoulou et al. (24) and Schmale et al. (25). This can be explained by the decreased concentration of \( \text{Pr}^{\text{Ce}}_{\text{Ce}} \) at elevated temperature which counteracts the increased mobility of the electron holes (24).

The total conductivity is insensitive to the change of oxygen partial pressure in the range from \( 1 \times 10^{-5} \) bar to 0.21 bar for Pr substitutions lower than 8 at.% whilst it shows detectable \( pO_2 \)-dependence for Pr concentrations larger than 15 at.% The \( pO_2 \)-dependence becomes more pronounced with increasing Pr concentration because the electronic conductivity is sufficient to influence the total conductivity and the ionic conductivity decreases with decreasing \( pO_2 \) (as shown in Fig. 10).

In Fig. 10, the oxide ion conductivities were obtained by subtracting the electronic conductivities from the total conductivities (see Fig. 9). It can be observed that the oxide ion conductivity is invariable over the \( pO_2 \) range for the samples doped with less than 15 at. % Pr but steadily decreases with decreasing \( pO_2 \) for the more heavily doped samples (>15 at. % Pr). As \( pO_2 \) decreases, the concentration of acceptor dopants increases because of the increasing \( \text{Pr}^{\text{Ce}}_{\text{Ce}} \) concentration. Oxygen vacancy concentration accordingly increases to counterbalance the increased charge of acceptor dopants. The unchanged (CGO, CPGO2, CPGO5 and CPGO8) or decreased conductivity (CPGO15, CPGO25, CPGO30 and CPGO40) with increasing \( pO_2 \) must be ascribed to a decreasing oxide ion mobility with increasing oxygen vacancy concentration and increasing concentration of \( \text{Pr}^{3+} \). One does, in terms of ionic conductivity not benefit from doping beyond the 10 at.% Gd. This is well in line with literature on optimal conductivity in acceptor doped ceria which typically points to a maximum in ionic conductivity at doping levels
between 10 and 20% (41). The maximum ionic conductivity in this doping level may be due to the tradeoff between the increased oxygen vacancy concentration and the development of deep vacancy association induced by electrostatic interaction. (3).

Fig.10 Logarithm of oxide ion conductivity versus log $pO_2$ for each composition. The lines were obtained by linear fitting to the data.

4.8. Calculated and measured oxygen permeation fluxes

Fig. 11 displays the calculated and measured oxygen flux for CPGO5, Co5CPGO5 and CGO as a function of temperature under a fixed oxygen partial pressure difference ($\ln(pO_2'/pO_2'')=7$). All samples in the flux measurements were coated on both sides with porous LSC layers (c.f.
The calculated fluxes were obtained from Wagner’s equation in terms of the measured electronic and ionic conductivity (see Fig. 9 and 10). It is noteworthy that the calculated flux is consistent with the measured flux. This indicates that the measured oxygen flux is limited by bulk ambipolar diffusion in the 1-mm thick pellet investigated rather than surface exchange. Another noticeable feature is that the oxygen flux of CPGO5 is higher than that of CGO by a factor of five at 900°C. It has previously been reported that cobalt oxide containing ceria based membranes show enhanced oxygen flux compared to the corresponding cobalt oxide free membrane because percolating cobalt oxide forms along the grain boundary enhancing electronic conductivity without influencing the ionic conductivity (17, 42, 43). The enhanced oxygen flux is reported to be due to the enhanced electronic conductivity. However, we did not observe enhanced flux for the cobalt-containing sample, instead the opposite trend was observed. The slightly decreased oxygen flux in cobalt oxide containing samples in this work may be due to the formation of discrete CoO_x-rich segregation at the grain boundaries resulting from the high sintering temperature (1200 °C) instead of forming a continuous percolating network as found in other studies (17, 42, 43).
5. Discussions

5.1. Electronic conductivity under oxidizing conditions

Praseodymium oxides (PrOₓ) exist in variable compositions (x in the range from 1.5 to 2) at elevated temperatures where the valence state of Pr thus varies between Pr³⁺ and Pr⁴⁺. As the reduction of Pr occurs, the electrical conductivity of PrOₓ significantly increases, up to a value of 1.4 Scm⁻¹ at 850 °C (44). The electrical conductivity of PrOₓ at high temperature is assigned to electronic conductivity, which originates from electron hopping between mixed-valence Pr³⁺/Pr⁴⁺ cations present in the lattice. Unlike PrOₓ, Gd-doped ceria is an oxide ion conductor with negligible p-type electronic conductivity under oxidizing condition. As observed (Fig. 8
and 9), a combination of PrO$_x$ and Gd-doped ceria; making a Pr/Gd co-doped ceria solid solution gives rise to mixed ionic-electronic conductivity.

The mechanism for the mixed ionic-electronic conductivity of Pr in ceria has been rationalized in many papers in terms of band theory. Stefanik et al. proposed that Pr-substitution for cerium forms discrete acceptor levels (Pr 4f) for the lightly doped ceria (below 10 at.%) (34, 35). The discrete states are not capable of giving rise to considerable electronic conductivity. Lübke et al. (13) proposed that the Pr 4f states lie much closer to the O2p valence edge than the Ce 4f conduction band. At sufficiently high temperature, electrons in the O2p state will be thermally excited and subsequently localized in the Pr 4f states, resulting in formation of holes in the valence band. Furthermore, at high temperatures and/or decrease $pO_2$, oxygen is released from the lattice increasing the electron occupation of the Pr 4f states. Here, we shall analyze the experimental results in a “chemical picture” relating the conduction to electronic defects associated with the Pr sites.

In several studies (17, 20, 25), it has been reported that the electronic conductivity of Pr-doped ceria can be well described by a small polaron mechanism. Hence, mobility and conductivity will scale with temperature according to (34):

$$\mu_{\text{polaron}} = \frac{(1 - [\text{Pr}^{3+}])e^2\nu_0}{kT} \exp\left(-\frac{E_H}{kT}\right)$$  \hspace{1cm} (18)

$$\sigma_{\text{polaron}} = N [\text{Pr}^{3+}] \mu_{\text{polaron}} e$$  \hspace{1cm} (19)

$$\sigma_{\text{polaron}} = N [\text{Pr}^{3+}](1 - [\text{Pr}^{3+}]) \frac{e^2 a^2 \nu_0}{kT} \exp\left(-\frac{E_H}{kT}\right)$$  \hspace{1cm} (20)

$$[\text{Pr}^{3+}] = \frac{[\text{Pr}^{3+}]}{[\text{Pr}^{3+}]+[\text{Pr}^{4+}]}$$  \hspace{1cm} (21)
where $\mu_{\text{polaron}}$ is the mobility of the small polaron, $\left[\text{Pr}^{3+}_{\text{Ce}}\right]$ is the fractional occupancy of electrons trapped on Pr ions. $\left[\text{Pr}^{3+}\right]$ is the concentration of trivalent Pr, $N$ is the volumetric density of Pr atoms in the material (mol cm$^{-3}$). $v_0$ is the jump frequency, $E_H$ is the activation energy for hopping of the electron hole (electron hole migration), and $a$ is the hopping distance. Eq. (20) can be rewritten to a simpler Arrhenius type expression:

$$\ln\left(\sigma_{\text{polaron}} T\right) = -\frac{E_H}{k} \frac{1}{T} + \ln C$$  \hspace{1cm} (22)

where $C$ is ($C = Ne^2 \left[\text{Pr}^{3+}\right] (1 - \left[\text{Pr}^{3+}_{\text{Ce}}\right]) k^{-1} a^3 v_0$). The electronic conductivity is thus influenced by both the concentration of Pr$^{3+}$ and Pr$^{4+}$. When the concentration of Pr$^{3+}$ prevails the material is a p-type conductor; where concentration of Pr$^{4+}$ prevails it becomes n-type. In the following discussion we concentrate on the p-type electronic conductivity which is typically observed under practically realizable conditions. For comparison of mobilities and activation energies between the compositions we shall compare data at a fixed Pr$^{3+}$/Pr$^{4+}$ ratio. The choice of 2.7 for Pr$^{3+}$/Pr$^{4+}$ ratio relates the available $pO_2$ range for achieving a fixed ratio at all temperatures for all compositions. The oxygen partial pressures in equilibrium with a fixed ratio of (Pr$^{3+}$/Pr$^{4+}$ $\approx$ 2.7 as observed by TGA) in the different samples are listed in Table 4.

**Table 4. Oxygen partial pressure for the fixed ratio between Pr$^{3+}$ and Pr$^{4+}$ ($\text{Pr}^{3+}/\text{Pr}^{4+} = 2.7$) of CPGO at 700, 800 and 900°C.**

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>900</th>
<th>800</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPGO40</td>
<td>1.70 bar</td>
<td>0.08 bar</td>
<td>9.0e-3 bar</td>
</tr>
<tr>
<td>CPGO30</td>
<td>0.76 bar</td>
<td>0.04 bar</td>
<td>5.6e-4 bar</td>
</tr>
</tbody>
</table>
Fig. 12A shows Arrhenius plots of electronic conductivity with a Pr\(^{3+}/\text{Pr}^{4+}\) ratio and corresponding linear fittings. The activation energies and pre-exponential constants of electronic conductivity obtained by linear fittings in Fig. 12A are shown in Figs. 12C and 12D, respectively. As indicated by Eq. 21, the activation energy in Fig 12C corresponds to the migration enthalpy of the electron hole whilst the pre-exponential factor is associated with the jump frequency \(v_0\), hopping distance \(a\) and doping level. A noticeable feature in Fig. 12B is that there is a marked change in the scaling of the logarithm of the conductivity versus the Pr concentration around 10 at.% Pr especially at low temperature. An abrupt decline of the activation energy (Fig. 12C) and pre-exponential factor (Fig. 12D) is observed in the same range.
Fig. 12 (A) Arrhenius plots of the electronic conductivity for CPGOx at a fixed Pr$^{3+}$/Pr$^{4+}$.

(B) Electronic conductivity as a function of dopant concentration from 500 °C to 1000 °C. Apparent activation energy and (D) pre-exponential factor of the electronic conductivity versus x obtained from the linear fitting in (A). The dotted lines are plotted to guide the eye. The vertical line indicates a percolation threshold for Pr in the structure (see text).

The Pr-doped CGO solid solutions can be viewed as PrO$_x$ clusters homogenously embedded in the Gd$_{0.1}$Ce$_{0.9}$O$_{1.95-\delta}$ matrix. Electronic charge carriers (electrons or holes) are localized preferentially in the PrO$_x$ units and migrate via them upon thermal excitation. For samples doped with low Pr concentration, the distance among the discrete PrO$_x$ clusters is relatively long imposing a high energy barrier for electrons to jump across the CeO$_2$/Gd$_2$O$_3$-based zones, which are electronic “insulating”. This results in low electronic conductivity and high activation
energy for $x<0.1$ samples, as shown in Fig. 12C. Furthermore, the high value of the pre-
 exponential constant for the $0<x<0.1$ samples is indicative of a long electron hole hopping
distance ($a$ in Eq. 19).

As the dopant concentration increases, the distance between the Pr ions decreases, resulting in
decreased effective hopping distance and decreased activation energy. The transient behaviour
in the range $0.08<x<0.15$ is akin to the percolation effect that is generally found in composite
materials consisting of an electrical conductor and an insulator. That is, the abrupt increase of
electrical conductivity occurs when the amount of the electrical conductor surpasses the
percolation threshold above which a continuous electrical conduction pathway penetrates all
the way through the composite. The same phenomenon is observed also in solid solutions.

Swider and Worrell (45) employed a percolation model to explain the n-type electronic
conductivity of Ti-doped YSZ. A theoretical percolation threshold of 12.5% for Ti-YSZ was
proposed on the basis of bond percolation in the crystal structure. Kim et al. (46) recently
developed a simple cubic percolation model to interpret the non-linear increment of electrical
conductivity in perovskite structured BaZrO$_3$-BaFeO$_3$ solutions. Generally, the percolation
threshold ($P_c$) for a close-packed crystal structure e.g. FCC is a function of the site coordination
number $Z$, and can be simply evaluated as (47)

$$P_c = \frac{1.5}{Z} \quad (23)$$

The shortest possible jump distance will be achieved when the electronic defect localized on a
given Pr dopant located on a corner of the cubic unit cell has at least one other Pr among the 12
nearest neighbour sites on the cubic face centres. A possible percolating Pr-Pr pathway is
illustrated in Fig. 13. The cation coordination number in the FCC structure equals 12 ($Z=12$ in
Eq. 23). Therefore, by the simple model described in ref. (47), the percolation threshold is
~12.5%, which means that the electronic defect may hop continuously among nearest Pr cations
when 12.5% of the cation sites are occupied by Pr. It is evident that the observed transition range (8 at.%-15 at.%) lies close to the one predicted by this simple percolation model. From the conductivity data plotted in Fig.12 it is evident that a strong correlation exists between the structural connectivity of the Pr dopants and the migration enthalpy for the electron holes.

Fig.13 Schematic illustration of a (100) plane of a 2×2 matrix. A possible percolation path of Pr-Pr nearest neighbours is also shown.

Due to the influence of activation energy and the pre-exponential factor, we herein plot the extrapolated conductivity at high temperature (e.g. 800°C) to pinpoint the abrupt change of electrical conductivity arising from the migration enthalpy. In Fig. 14, the extrapolated electronic conductivity at 800 °C was fitted by the percolation model proposed by Kim et al. (46). In this model, the conductivity for x<Pc and x>Pc is phenomenologically described by the expressions:
For $x < P_c$, $\sigma(x) = \sigma_{CGO} x^{t/2} (P_c - x)^{-s}$ \hfill (24)

For $x > P_c$, $\sigma(x) = \sigma_{PrO_x} (x - P_c)^t$ \hfill (25)

where $s$ and $t$ are the universal size scaling exponents for the non-percolation matrix and the percolation phase, respectively. $\sigma_{CGO}$ and $\sigma_{PrO_x}$ are the electronic conductivities of CGO and PrO$_x$ at 700 °C, respectively. $P_c$ is the percolation threshold being treated as a fitting parameter. $s$ and $t$ are the two fitting parameters where $t$ is theoretically limited to lie in the range from 1.65 to 2 for the simple cubic percolation model. The best fit of the model to the data in Fig. 14 gives $t = 1.80$, $P_c = 0.125$ and $s = -1.11$, with the $R^2$ equals to 0.93. The model seems to satisfactorily fit the data in this work, which further elucidates that the electronic behavior can be well explained by the percolation model.
Fig. 14 Electronic conductivity (fixed Pr\(^{3+}/Pr^{4+}=2.7\)) at 800 °C as a function of x. The data is fitted with a simple cubic percolation with charge carriers donated by dopants (Eq.24 and 25). The percolation threshold (P\(_c\)) is estimated to be x≈0.13 in the fitting. The electronic conductivity of CPGO10 (Pr\(_{0.1}\)Gd\(_{0.1}\)Ce\(_{0.8}\)O\(_{1.95}\)) and PrO\(_x\) are taken from ref.(25) and ref. (44), respectively.

5.2. Chemical expansion (CE) under oxidizing conditions

The chemical expansion of CGPO is related to the volumetric dilation upon changes in oxygen stoichiometry. The cell lattice parameter expands with the increase of the concentration of Pr\(^{3+}\). Chatzichristodoulou et al.(37) has estimated that when relating unit cell volumes to the ionic
radii of the constituting ions the size of an oxide vacancy in fluorites is smaller than that of the oxide ions. The chemical expansion of CPGO is thus in this picture a consequence of lattice dilation due to the increased radius of the cations partially counterbalanced with oxygen vacancy induced lattice contraction. The lattice parameter as calculated by Kim’s formula includes the sum of the two effects. The relative chemical expansion can be simply calculated by a Vegard’s law type relationship between lattice dimension and fraction of Pr$^{3+}$ or Pr$^{4+}$ in CPGO:

$$
\varepsilon_{\text{cal,chem}} = \frac{[\text{Pr}_\text{Pr}'] a_{\text{Pr}^{3+}} + \left(1- [\text{Pr}_\text{Pr}'] \right) a_{\text{Pr}^{4+}} - a_{\text{XRD}}}{a_{\text{XRD}}} (26)
$$

where $a_{\text{Pr}^{3+}}$ and $a_{\text{Pr}^{4+}}$ are the calculated lattice parameters for only Pr$^{3+}$ or Pr$^{4+}$ in CPGO, respectively (see Fig. 5). $a_{\text{XRD}}$ is the lattice parameter obtained by XRD refinement (cf. Fig. 6), $[\text{Pr}_\text{Pr}']$ is the fraction of Pr$^{3+}$ calculated by the thermodynamic parameters outlined in Table 2. Fig. 15 shows the relative chemical expansion (CE) from the experimental dilatometry data and the CE calculated by Eq. 24, respectively. Overall, the calculated CE in this simple model reproduces the general trend of the experimentally deduced CE well. Note that Eq. 26 is consistent with a type of expression as Eq. 16 i.e. it predicts proportionality between $\varepsilon_{\text{chem}}$ and $\delta$.

A transition is seen experimentally around 12.5% Pr. Below this the chemical expansion is small, above stronger. There are three reasons for this as seen when comparing the experimental data to the curve calculated from Eq. 26 and considering the $\Delta H$, $\Delta S$ and $\beta$ values reported in Tables 2 and 3. Firstly; the overall expansion will increase with the fraction of the cation sites that are occupied by Pr (Fig. 5). Secondly, for a given $T$, $pO_2$ condition (900°C, air) the fraction of the Pr that is reduced increases with increasing Pr concentration.
Thirdly, there is a weak tendency that above the percolation threshold the lattice responds even stronger to the change in ionic radius than below the threshold. The experimental data lies above the Eq. 26 trend line for $x=15$, 25 and 30 but below for $x=8$. It should be noted, that the relative chemical expansions listed in Fig.15 are estimates only and thus encompassed with some uncertainties. They are derived from the measured total expansion (well determined) by subtracting an estimated thermal expansion, which is calculated under assumption of a constant thermal expansion coefficient ($\alpha$) (see discussion in section 4.5).

Besides the uncertainty introduced by this assumption, the data for the low Pr contents may be encompassed with an uncertainty due to incomplete equilibration with the atmosphere during the temperature sweeps. For these samples full oxygen equilibration, which is limited by electronic conductivity, might not have been achieved at the given cooling rate. This would add to exaggerate the change in behavior around the percolation threshold.
566 Fig. 15 Dependence of relative chemical expansion on $x$ in $\text{Pr}_x\text{Gd}_{0.1}\text{Ce}_{0.9-x}\text{O}_{1.95-\delta}$. Calculated values of relative chemical expansion using Kim's formula in conjunction with thermodynamic parameters are also shown. The value of $\text{Pr}_{0.1}\text{Gd}_{0.1}\text{Ce}_{0.8}\text{O}_{1.95}$ calculated by Heidenreich et al. (48) is also included.

567

5.3. Electronic conductivity under reducing conditions

568 Consistently, all the samples show n-type electronic conductivity under reducing conditions ($<1 \times 10^{-15}$ bar). The n-type regime is associated with partial reduction of $\text{Ce}^{4+}$ as described in Eq. 4. However, for the samples with high Pr concentration, the n-type electronic conductivity is partly overshadowed by the considerable p-type electronic conductivity (Fig. 9). The “net” n-type electronic conductivity at a given $\text{pO}_2$ ($1\times10^{-15}$ bar) is thus obtained by subtracting the
extrapolated p-type electronic conductivity based on the slope of the p-type at high pO₂ branch from the total electronic conductivity. It is observed that the apparent activation energy of “net” n-type electronic conductivity decreases with increasing Pr concentration. Lübke et al. (13) found a slight decrease of the activation energy in CGO doped with 3 at.% Pr relative to that in CGO. Navarro et al. (49) also found that the 2 at.% Pr-doped CGO20 shows slightly decreased n-type conductivity relative to CGO20, in agreement with our results. In contrast to the trend observed in the pO₂ range dominated by p-type electronic conductivity, the n-type electronic conductivity under reducing conditions steadily decreases with increasing Pr concentration. The decrease of n-type electronic conductivity is more pronounced at high temperature (900 °C). It is generally agreed that the n-type electronic conductivity in ceria is correlated with the electron hopping on the ceria sites (Ce³⁺/Ce⁴⁺). The mobility will thus be proportional to the concentration of Ce (22). Here, partial substitution of Pr for Ce decreases the concentration of ceria (Ce³⁺/Ce⁴⁺), accounting for the lower n-type electronic conductivity because of the decreased number of sites. Under strongly reducing conditions, Pr⁴⁺ is completely reduced to Pr³⁺ which increases the oxygen vacancy concentration owing to the summation of now two acceptor dopants ([PrCe] and [GdCe]). The high oxygen vacancy concentration is further unfavourable to the electron migration (50, 51), resulting from the more severe association between Ce’Ce and V̅O upon a larger oxygen vacancy concentration (52). This effect also contributes to the reduction of the n-type conductivity in the Pr-containing samples.

The activation energy of the n-type electronic conductivity was also observed to decrease with increasing Pr concentration. The apparent activation energy is composed of two terms: $E = H_m + \frac{1}{4} H_{ce}$ where $H_m$ is the enthalpy of electron migration and $H_{ce}$ is the standard reaction enthalpy. According to literature (52), the enthalpy of electron migration increases with increasing oxygen vacancy concentration in ceria. Although $H_m$ of the materials in this work is
not known, increased $H_m$ values are expected with increasing Pr concentration. This indicates that Ce will be more readily reduced upon a higher Pr concentration. A similar trend was also observed in purely Pr-doped ceria (35) and purely Gd-doped ceria (53). It is also found that the reducibility of Ce$^{4+}$ and Pr$^{4+}$ in ceria tends to be facilitated by the increasing oxygen nonstoichiometry, leading to a non-ideal reduction behaviour (16). We herein attribute the decreased enthalpy of reduction of Ce to the high oxygen nonstoichiometry in heavily Pr-doped CGO.

![Fig. 16](image)

Fig. 16 (a) $n$-type electronic conductivity of CPGO under $pO_2=1\times10^{-15}$ bar as a function of $x$ at 700, 800 and 900 °C. (b) Apparent activation energy of the electronic conductivity under $pO_2=1\times10^{-15}$ bar.

5.4. Ionic conductivity

For Pr and Gd co-doped ceria, more oxygen vacancies will form to compensate the increased concentration of negatively (compared to Ce$^{4+}$) charged aliovalent dopants ($Pr_{Ce}$ and $Gd_{Ce}$). In analogy with purely Pr-doped or Gd-doped ceria (3), the ionic conductivity of Pr and Gd co-doped ceria does not monotonously increase with increasing oxygen vacancy concentration as illustrated in Fig.17. Instead, a maximum ionic conductivity occurs around an acceptor dopant
concentration of 25 at.% (11.4 at% Pr$^{3+}$, 3.6 at.%Pr$^{4+}$, 10 at.% Gd and volumetric oxygen vacancy concentration equals to 1.07×10$^{22}$ cm$^{-3}$). According to Dholabhai’s DFT calculations (54), 20 at. % dopant content in ceria shows the maximum ionic conductivity for 10 at.% Pr and 10 at.% Gd co-doped ceria, in good agreement with the experimental results in this work. Another noticeable feature is that the decrease of oxide ion conductivity above 25 at.% is associated with an increase in the apparent activation energy. The large activation energy of the electrical conductivity in heavily acceptor doped ceria is observed in several studies (3, 55). It is likely due to the association between the extrinsic dopants and oxygen vacancies (55);

\[ 2\text{Acc}_{\text{Ce}} + V_{\text{O}}^{\ast\ast} \rightarrow \left[ \text{Acc}_{\text{Ce}} V_{\text{O}}^{\ast\ast} \text{Acc}_{\text{Ce}} \right] \text{ or} \]

\[ \text{Acc}_{\text{Ce}} + V_{\text{O}}^{\ast\ast} \rightarrow \left[ \text{Acc}_{\text{Ce}} V_{\text{O}}^{\ast\ast} \right] \]

where $\text{Acc}_{\text{Ce}}$ represents the acceptor dopants Gd$^{3+}_{\text{Ce}}$ and Pr$^{3+}_{\text{Ce}}$ whereby some of the oxygen vacancies are trapped by the immobile dopants. As illustrated in Fig. 17, where the data for several different acceptor doped ceria compounds are compared, the defect association results in an increased apparent activation energy for oxide ion conductivity for the heavily doped samples.
Fig. 17 Apparent activation energies of oxide ion conductivity in pure N$_2$ (pO$_2$≈0.001 bar) as a function of Pr content. The lines were plotted to guide the eye. Inset: The oxide ion conductivity measured at 800 °C as a function of acceptor dopant concentration for different ceria solid solutions from (35, 56, 57). The ratio of Pr$^{3+}$/Pr$^{4+}$ at 800 °C in N$_2$ is in the range of 4-9.

5.5. Oxygen permeation flux

The maximum achievable oxygen flux occurs when the oxide ion and electronic conductivity in a MIEC are both high and equal (transport number=0.5). As shown in Fig 18a where calculated transport numbers are shown, the transport number of CPGO approaches to 0.5 when the Pr concentration is in the range from 30 at.% to 40 at.%. Shuk et al. (58) also found nearly equal electronic and ionic conductivity for Pr$_{0.3}$Ce$_{0.7}$O$_{1.85-δ}$ at 700 °C, in good agreement with
this work. The maximum achievable theoretical oxygen permeation flux can be calculated in terms of electronic and ionic conductivity using the Wagner’s equation:

\[
J_{O_2} = \frac{RT}{16F^2L} \ln \frac{p_{O_2}^e}{p_{O_2}^i} \int \frac{\sigma_e \sigma_i}{\sigma + \sigma_i} \partial \ln p_{O_2}
\]  

(27)

The calculated oxygen permeation flux (here any losses at the two surfaces are neglected) follows the trend of \( \tau_e \) (Fig. 18b), due to the fact that the oxygen permeation flux of \( \text{Pr}_x\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95-\delta} \) is dominantly limited by the electronic conductivity until a Pr concentration of approximately 40 at.%, where the maximum oxygen permeation flux is predicted for the here considered composition range (0-40 at. % Pr). Despite the reduced ionic conductivity when exceeding 25at.% doping concentration, considering the bulk diffusion exclusively, the maximum oxygen flux for a 10-µm thick \( \text{Pr}_{0.4}\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95-\delta} \) based membrane may reach up to 10 Nml cm\(^{-2}\) min\(^{-1}\) at 800 °C under the driving force of 0.21 bar/0.001 bar approaching the required level for being commercially interesting (59). However, the considerable chemical expansion of CPGO40 (Fig. 7) is a severe challenge in terms of ensuring mechanical integrity and limits the applicability of the material (8). To reduce risks of mechanical failure originating from chemical strain, very low thickness (1-10 µm) would be needed and the oxygen pressure gradient over the materials should be carefully controlled. A discussion of the consequence of chemical strain in supported membrane architectures can be found in ref. (60-63).
Fig. 18 (a) Calculated transport number and (b) calculated oxygen permeation flux as a function of x in Pr$_x$Gd$_{0.1}$Ce$_{0.9-x}$O$_{1.95-\delta}$ at 700, 800 and 900 °C.

6. Conclusions

The investigations of the transport properties of Pr,Gd-doped ceria presented here has led to the following conclusions;

1. Doping Pr in CGO (Pr$_x$Gd$_{0.1}$Ce$_{0.9-x}$O$_{1.95-\delta}$) significantly enhances the electronic conductivity (0.04 Scm$^{-1}$ for Pr$_{0.4}$Gd$_{0.1}$Ce$_{0.5}$O$_{1.95-\delta}$ vs. 5.6×10$^{-4}$ Scm$^{-1}$ for Gd$_{0.1}$Ce$_{0.9}$O$_{1.95-\delta}$ at 900 °C when $p$O$_2$=0.21 bar) under high oxygen partial pressures ($p$O$_2$>10$^{-8}$) and decreases slightly the n-type electronic conductivity (0.03 Scm$^{-1}$ for Pr$_{0.4}$Gd$_{0.1}$Ce$_{0.5}$O$_{1.95-\delta}$ vs. 0.3 Scm$^{-1}$ for Gd$_{0.1}$Ce$_{0.9}$O$_{1.95-\delta}$ at 900 °C when $p$O$_2$=1×10$^{-15}$ bar) under low oxygen partial pressures ($p$O$_2$<10$^{-8}$).

2. Doping Pr in CGO (10 at.% Gd) leads to a slight enhancement of the maximum oxide ion conductivity when the total dopant concentration is lower than 30 at.% (0.083 Scm$^{-1}$ for Pr$_{0.15}$Gd$_{0.1}$Ce$_{0.75}$O$_{1.95-\delta}$ vs. 0.067 Scm$^{-1}$ for Gd$_{0.1}$Ce$_{0.9}$O$_{1.95-\delta}$ at 800 °C when $p$O$_2$=1×10$^{-3}$ bar).

3. The apparent thermal expansion increases with increasing Pr concentration, due to increased chemical expansion (14.5×10$^{-6}$ K$^{-1}$ for Pr$_{0.05}$Gd$_{0.1}$Ce$_{0.85}$O$_{1.95-\delta}$ vs. 12.5×10$^{-6}$ K$^{-1}$ for Gd$_{0.1}$Ce$_{0.9}$O$_{1.95-\delta}$ in the range from 200 °C to 900 °C). The chemical expansion coefficient varies in the range from 0.05 to 0.09.

4. The enthalpy of the Pr$^{4+}$ to Pr$^{3+}$ reduction reaction decreases with increasing Pr concentration (112±10 kJ mol$^{-1}$ for Pr$_{0.4}$Gd$_{0.1}$Ce$_{0.5}$O$_{1.95-\delta}$ vs. 200±34 kJ mol$^{-1}$ for Pr$_{0.08}$Gd$_{0.1}$Ce$_{0.82}$O$_{1.95-\delta}$).
5. An abrupt decrease of the electron hole migration enthalpy is observed when the Pr concentration increases from 8 to 15 at.%, which is likely associated with the establishment of a percolation path between the Pr atoms as the chance of finding a continuous path of Pr atoms in the nearest neighbour positions strongly increases at this substitution level. The percolation threshold can be interpreted in a simple cubic percolation model.

6. No beneficial effect of adding 3% Co to the achievable permeation flux is observed but the Co is found to be a good sintering aid.

7. The Gd/Pr co-doped material may be applied in composite electrodes (SOFC cathodes) where the simultaneous increase in ionic and electronic conductivity on Pr substitution in the CGO will be beneficial and the large chemical expansion may be tolerable if only used in nanoparticulate form. The large chemical expansion introduced by the co-doping limits application for membranes, as to bring the electronic conductivity in the range of the ionic one needs more than 12.5 at.% Pr addition, which also makes the material prone to problems related to the large chemical (stoichiometric) expansion.

8. The achievable oxygen permeation flux of CGO is enhanced by co-doping with Pr because of the enhanced electronic conductivity. CPGO40 is predicted to show the largest achievable flux as the electronic conductivity approaches the ionic one. As a trade-off, CPGO5 is a promising material for OTMs in terms of enhanced oxygen flux and low chemical expansion.

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References
