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# Oxygen permeability of mixed-conducting $Ce_{0.8}Tb_{0.2}O_{2-\delta}$ membranes: Effects of ceramic microstructure and sintering temperature

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ABSTRACT

Nanopowder of $Ce_{0.8}Tb_{0.2}O_{2-\delta}$, a fluorite-type mixed conductor stable in wide $p(O_2)$ range, was successfully synthesised by the hydrothermal method. Dense ceramics sintered at relatively low temperatures (900 and 1200 °C), by employing minor additions of cobalt oxide sintering additive (2 mol%), were compared to those sintered at 1500 °C without additives. The effect of the sintering temperature on oxygen transport was analysed in $O_2$ and $N_2$ atmospheres. Oxide-ion transference numbers were determined by the modified electromotive force (EMF) method under oxygen/air and nitrogen/air gradients, showing positive temperature dependencies for all sintering temperatures. The partial ionic and electronic conductivities, calculated from the transference numbers and total conductivity, both increase with cobalt additions. A detailed transmission electron microscopy (TEM) study shows a grain boundary location of the cobalt sintering additive at the lowest sintering temperature, 900 °C. On increasing sintering temperature the grain-boundary concentration of cobalt is depleted, leading to the presence of segregated grains of cobalt oxide. This factor is shown to be highly relevant with respect to measured oxygen permeation fluxes. $Ce_{0.8}Tb_{0.2}O_{2-\delta}$ ceramics sintered at 900 °C show significantly higher oxygen permeation, related to improved surface exchange due to the grain-boundary enrichment of cobalt and larger grain-boundary area.



## 1. Introduction

Recently, mixed ionic–electronic conductive (MIEC) materials have been studied for many applications like solid oxide fuel cells (SOFC) [1], three-way catalysts [2], oxygen sensors [3], oxygen permeation membranes [4] and ultraviolet ray absorbents [5]. Mixed conductivity is an attractive property for SOFC cathodes due to enlargement of the electrochemical reaction zone, subsequently lowering polarisation losses [6]. In the case of practical oxygen separation membranes, the perovskite-type mixed ionic–electronic conductive materials $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) and $La_{0.5}Sr_{0.5}Fe_{1-x}Co_xO_{3-\delta}$ (LSFC) have shown high oxygen permeability and attractive methane conversion characteristics [7,8]. However, the main disadvantages of these oxides are their high thermal and chemical expansion coefficients and low chemical stability [9,10]. Fluorite-type doped cerium oxides are another important class of MIEC materials due to their high rates of oxygen exchange, diffusion and good stability in repeated redox cycles [11–13]. In reducing conditions, ceria based oxides show extensive mixed conductivity via small polaronic hopping due to partial reduction of $Ce^{4+}$ to $Ce^{3+}$ [14]. Increased oxygen permeation fluxes in oxidising conditions can also be obtained by doping ceria with multivalent cations like Tb and Pr [15]. Thus, terbium-doped ceria is a promising MIEC fluorite material in both reducing and oxidising atmospheres that has gained recent interest [16]. Physical and chemical properties of $Ce_{1-x}Tb_xO_{2-\delta}$ have been reported by various authors [17–20], while total, ionic and electronic conductivities of $Ce_{1-x}Tb_xO_{2-\delta}$ ($x$=0–0.30) have been provided by Shuk et al. [21]. In general, the total conductivity was shown to increase with increasing Tb content, a trend that was later corroborated by Ye et al. across the whole composition range ($x$=0.00–1.00) [22]. For doping levels $x$=0.15–0.25, Shuk et al. showed that ~50% electronic contribution to total conductivity was provided at 600–700 °C in oxidising conditions, corresponding to the ideal weighting of ionic and electronic conductivities to attain maximum ambipolar conductivity.

To avoid high sintering temperatures in ceria-based materials many researchers have investigated the addition of small quantities of transition metal oxides as potential sintering additives [23–26].

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With respect to terbium doped ceria, Balaguer et al. [16,27] reported that 2 mol% addition of cobalt oxide into $Ce_{1-x}Tb_xO_{2-\delta}$ could improve densification during sintering and could also significantly enhance the total and ambipolar conductivities over that of the Co-free oxide [27]. The observations of Balaguer et al. [16,27] concur well with those reported previously for other doped ceria materials, such as Gd or Pr-doped analogues, $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ and $Ce_{0.8}Pr_{0.2}O_{2-\delta}$, containing equal fractions of Co additive [28–32]. In the case of the Pr and Gd analogues, enhancements in ambipolar conductivity have been related to the presence of a Co network localised at the grain boundary, which can enhance available levels of electronic conductivity [28–32]. In contrast, Balaguer et al. [16,27] noted that a similar grain boundary location of Co was not observed in samples of $Ce_{1-x}Tb_xO_{2-\delta}$+Co ($x$=0.1, 0.2) sintered at 1300 °C. Nonetheless, substantial enhancements in ambipolar conductivity could still be obtained. Concerning this observation, it is important to note that improvements in mixed conductivity and faster oxygen exchange have also been outlined for ceria-based materials when the grain size has been reduced to the submicron range [33,34].

Thus, the idea behind the current work is to assess the enhancement of ambipolar conductivity in Co containing $Ce_{1-x}Tb_xO_{2-\delta}$ materials and to examine potential links between this behaviour, the resultant oxygen permeation and microstructural factors, with careful attention to the physical location of the sintering additive. In this respect, the sintering temperature has been documented to be an important factor that can negatively impact levels of ambipolar conductivity in the Gd and Pr analogues, when Co containing samples were sintered in excess of 900 °C [28,35–37]. In this work, we analyse the influence of sintering temperature on $Ce_{0.8}Tb_{0.2}O_{2-\delta}$ materials (CTO) containing 2 mol% additions of cobalt oxide sintering aid, through structural and microstructural characterisation, conductivity measurements, electromotive force (EMF) and oxygen permeation studies, in order to further understand the behaviour of these additives on the properties of CTO MIECs.

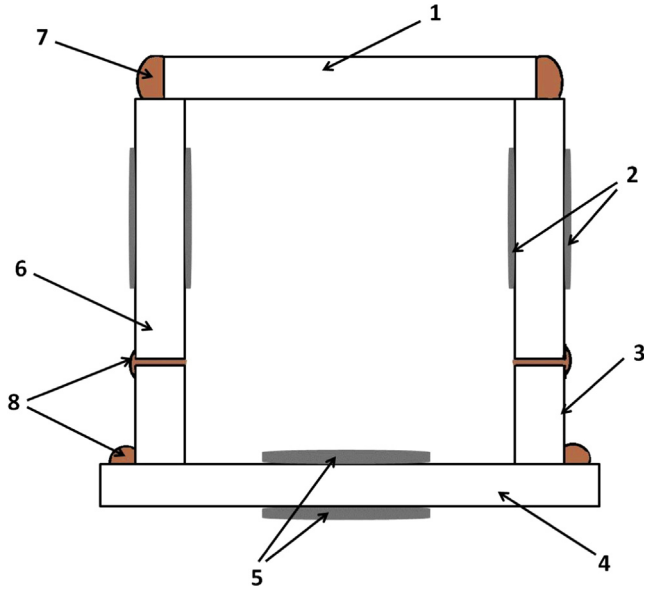


**Fig. 1.** Schematic drawing of the electrochemical cell for oxygen permeability measurements: (1) sample, (2) electrodes of the oxygen sensor, (3) YSZ tube, (4) YSZ tube (pump), (5) electrodes of the oxygen pump, (6) YSZ tube (sensor), (7) low-temperature glass, (8) high-temperature glass.

## 2. Experimental section

Cerium–terbium oxide ($Ce_{0.8}Tb_{0.2}O_{2-\delta}$) materials were prepared by the hydrothermal method, using cerium (III) nitrate hexahydrate

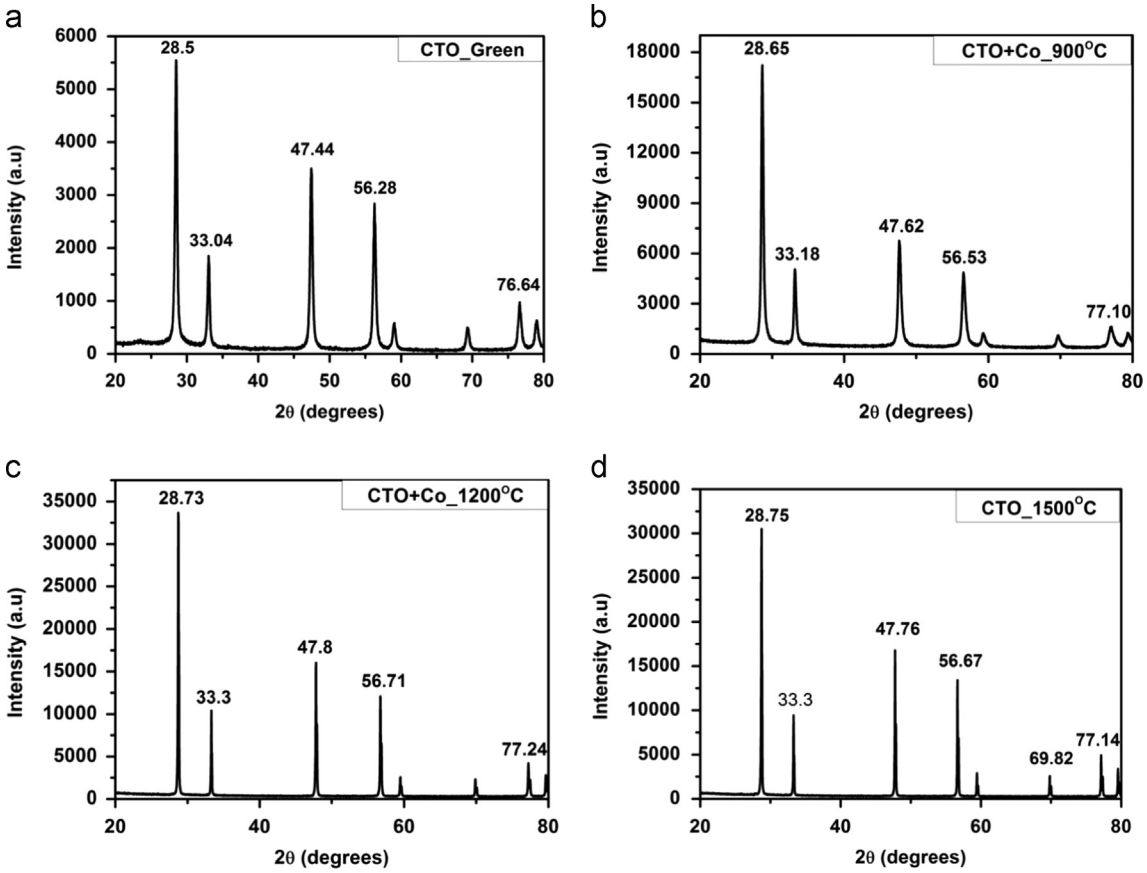


**Fig. 2.** X-ray diffraction patterns of as-prepared (a) pure $Ce_{0.8}Tb_{0.2}O_{2-\delta}$ and sintered Co-doped (b, c) and pure (d) $Ce_{0.8}Tb_{0.2}O_{2-\delta}$.